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Controlling Arsenic Accumulation in Rice Grain under Nanomaterials-Assisted Optimal Greenhouse Set-Up

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Abstract: Rice is being increasingly exposed to inorganic arsenic and this affects half of the world population because they are rice consumers. In this study, pot experiments were carried out to investigate the effect of two dose-dependent nanomaterials (silica and graphene) treatment on varied arsenic levels (2, 7 and 12 mg/kg). The results showed that both nanomaterials were affected significantly with 1 mg/mL of nanomaterial. Arsenic adversely affected the plant height, tillering, number of grains, and grain weight and when high concentrations of arsenic were applied at 12 mg/kg, the plant could not withstand it and died before 75 days even in the presence of graphene. Based on inductively coupled plasma mass spectrometry analysis, silica nanoparticles showed the highest inhibition on the total accumulation of arsenic as 93% (control plant), 84% (2 mg/kg), 67% (7 mg/kg) to 35 % (12 mg/kg), whereas graphene showed lower inhibition percentages. This outcome confirms that silica nanoparticles prevent arsenic uptake, because they translocate from the root to the grains and are able to offer a promising way to reduce consumer health risk.

Keywords: paddy plantation; rice straw; nanomaterial; metalloid

1. Introduction

The accumulation of heavy metals in agricultural land and its subsequent transfer to plants is a growing concern for the public, especially the rice paddy system, which largely depends on the soil for its nutrients. This raises the possibility of heavy metal bioaccumulation in humans. Using two novel nanomaterial approaches, this study aimed to monitor and control the heavy metal content of paddy soils, targeting the arsenic present in rice.

Today, almost half of the world's population consumes rice as a source for carbohydrates and due to the importance of rice a good deal of research has been carried out to secure and sustain rice production [1–5]. Recently, due to global warming and climate change, arsenic contamination has become a crucial issue that has hampered paddy plantations and yields, which is a side-impact not only for plants and animals but also for humans through the food chain. Rice plants have become more severe in term of arsenic accumulation compared to other crops, due to the pathway in the rice plant to uptake arsenic from the soil and the water used for irrigation. Furthermore, the rice plant contains a high affinity with phosphate/arsenate to drive arsenic from the root zone to the grains [6].

Arsenic is naturally abundant in the Earth's crust and is found either as an inorganic or an organic substance. In this case, the high availability of inorganic arsenic in the soil is caused by both the geography of the Earth and human activities such as mining, heavy usage of pesticides, herbicides, and insecticides in ritual agricultural activities [7]. Today, people are easily exposed to inorganic arsenic compared with organic arsenic by consuming large amounts of of seafood. Inorganic arsenic is referred to as a highly toxic metalloid that has a severe impact on human health in the form of chronic diseases such as cancer and skin disease, and has a genotoxic effect due to easier exposure through the consumption of water or food that were contaminated with arsenic. Even though arsenic concentration is low in grains due to adsorption by other parts of the plant, it still exhibits as a significant source of arsenic to be consumed by humans [8].

Several natural types of arsenic toxicity have been found in rice plants, namely arsenite, arsenate, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). However, a previous study has claimed that all the above are contained mainly in rice grains, and that MMA is rarely detected [9]. Due to high-risk pollution and public health issues, the highest permissible concentration is set by the World Health Organization (WHO), and has been recommended through appropriate and strict legislation. As a new order released by the WHO, the provisional acceptable weekly limit of inorganic arsenic intake in the human diet is not more than 15 $\mu g\ kg^{-1}$ of the body weight and it has endorsed a new standard regulation on the limitation of available inorganic arsenic in rice grains for the safety of the consumer as not >0.2 $mg\ kg^{-1}$ [10]. This was followed by a law adopted by the European Union where the legal and safe limit for rice grains to be consumed by adults was set as well as a limitation for infants of not >0.1 $mg\ kg^{-1}$ [11].

Considering the global implications of arsenic contamination and its impact on paddy development, researchers have been involved in preparing and using nanostructured adsorbent as an effective treatment. This is due to the fact that the nanostructure possesses a massive surface area with an average size below 100 nm [12]. This nanoscale structure has enormous potential due to its high efficiency and rapid pace, particularly in the removal of heavy metal such as arsenic. Furthermore, due to the abundant resources of agriculture waste as a biomass such as paddy straw, it can be utilized to produce novel nanomaterials such as silica nanoparticles and graphenes, which are known to have immense potential for reducing the arsenic accumulation in the greenhouse pot experiment [13–15]. Therefore, the discovery of novel nanomaterials from available sources of agricultural products will contribute to environmentally sustainable production and yield potential benefits.

As a result of global challenges related to environmental contamination and free competition to obtain nanostructured materials in comparison with other methods, the path towards environmentally friendly materials through economic potential is becoming increasingly popular and is a necessity. This is due to the fact that the route is becoming a necessity as a result of global challenges. In contrast to the synthesis of chemicals, the utilization of nanoparticles can be achieved through the use of materials from the "green path" that are not harmful to the environment. These eco-friendly materials are characterized by their easy procedures and straightforward instruments, as well as by their commitment to producing as little refuse as possible and adhering to other ecologically responsible practices [16].

There is a need to explore suitable alternatives to reduce arsenic accumulation in the rice plant. In this study, greenhouse pot experiments were conducted to investigate the accumulation of arsenic in various soil samples with different arsenic concentrations. In order to promote the application of nanomaterials to prevent the high accumulation of arsenic in rice grains, silica nanoparticles and graphene were used for the treatment. In this research, the influence and growth parameters were considered, and recommendations were suggested for the application of nanomaterials to reduce arsenic accumulation in paddy plants.

2. Materials and Methods

2.1. Adsorption Study on Silica Nanoparticle/Graphene

Plants such as rice have highly efficient mechanisms to uptake the required nutrients from the soil. Soil-essential nutrients are absorbed in proportion to their concentration levels. Because they support and aid various chemical reactions based on redox reactions, roots play an important role in plant nutrient absorption. These two reactions help solubilize and take up nutrients from the soil. When plants take the them up, they store the excess nutrients. These processes are repeated where the uptake, translocation, and storage are performed. Unfortunately, rice contains many toxic elements, such as arsenic. When humans consume rice, this results in the direct transfer of heavy metals to the human body. On the other hand, the mechanism of graphene and the reaction of silica nanoparticles and graphene to inhibit the accumulation of arsenic are extensively presented in various literatures. For example, Zulkafflee and Gang presents the detailed adsorption mechanism, adsorption dynamics, and isotherms of graphene heavy metal absorption in water. Moreover, another study presented the mechanism of silica heavy metal absorption; they proposed that silicon surface functionalization regulation, morphology, and structure control will enhance the heavy metal adsorption capacities of silica-based nanomaterials [17–19]. The absorption process is presented in detail below.

2.2. Adsorbent Dose Effect Analysis for Heavy Metal Removal

Determination of Arsenic

Initially, the arsenic solution contains a known concentration (12 mg/mL) as a stock solution is prepared as compared with a previous preliminary study [20]. Some 600 mg of As2O3 powder was weighed correctly and diluted directly in 50 mL of distilled water. The solution was then mixed well with a magnetic stirrer. At this point, various concentrations were prepared by diluting them in distilled water. The arsenic solution after dilution in distilled water becomes colorless. In addition to this, the adsorption analysis for arsenic using spectrophotometry was tested by the addition of variamine blue salt dye and followed the previously stated method [21].

In this analysis, the adsorbent dose responses of arsenic were experimentally determined using silica nanoparticles and graphene. For this analysis, several concentrations of nanomaterials (silica and graphene) were desired (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 mg/mL). Initially, 1 mg/mL of arsenic was prepared as a standard solution and poured into the conical flasks. This standard was tested against individual concentrations nanomaterials (silica and graphene). Each sample was then sonicated for 10 min and kept at 30 °C for 1 h. Next, samples were centrifuged to separate the pellets. One milliliter from each mixture was taken and added to 1 mL of KlO_3 and HCL, and subsequently shaken continuously until a yellow color appeared. After that, 1 mL of variamine blue base dye was added followed by 2 mL of sodium acetate, where the final violet color complex appeared. The absorption of heavy metal was spectrophotometrically determined. The percentage of removal from the initial and final arsenic amounts was determined.

2.3. Field Experimental Screening for Arsenic Toxicity in Selected Paddy Fields

All the sampling sites for rice grains are located in nine different places around Perlis, Malaysia. Located in the north of Malaysia, all samplings of rice plant with grains were collected at the matured stage at ~4 months after being planted. This period is the correct time to determine the concentration of arsenic. The selected locations for the study are shown in Figure 1a. The rice plants with grains were cut using scissors and kept in a clean plastic transparent bag. All samples were preserved in a chiller if they were not required for the analysis, thereby ensuring that they did not wither. Briefly, all were separated from the rice plant and washed in deionized water. Approximately 1.3 g of grain was weighed and ruined into small pieces and placed in conical flasks. Next, the samples were heated with 15 mL of nitric acid followed by 5 mL of perchloric acid at 90 °C. A yellowing color was observed at this stage and all the samples needed to be warmed and filtered. All the filtered solutions were diluted with 50 mL of distilled water and prepared for ICP-MS analysis.

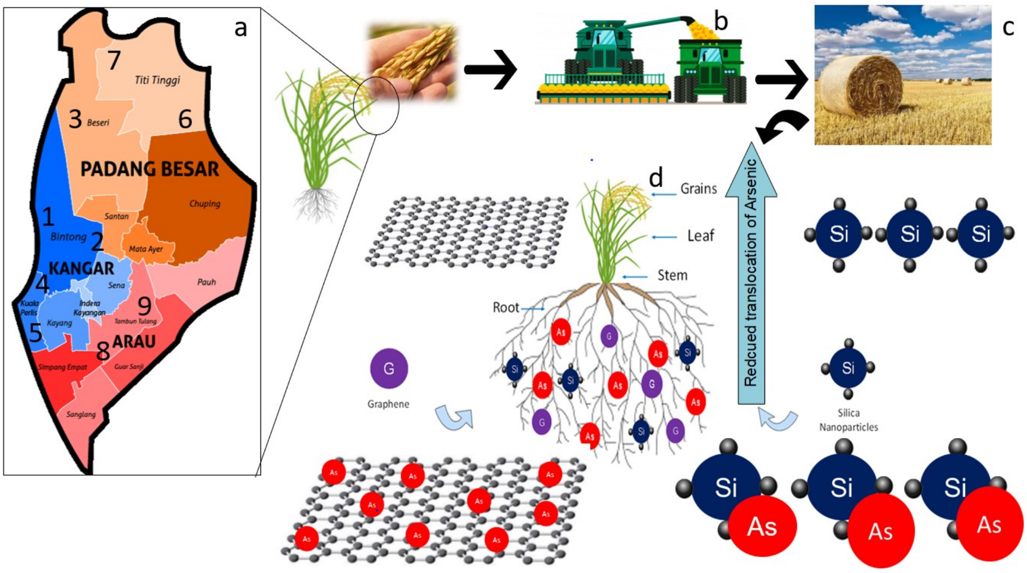


Figure 1. (**a**) It show the map and sample point where the arsenic were collected around paddy fields in Perlis. In this analysis, rice grains were collected and underwent grain digestion before we proceeded with an ICPMS measurement. (**b**) An illustration of the harvester used to harvest the matured paddy and leave behind the rice straw. (**c**) Rice straw used as the main precursor material for silica nanoparticle and graphene production. (**d**) Mechanism reaction on how nanomaterial acts as adsorbent reacts with arsenic. Due to the high surface area of both nanomaterials, the toxicity of the arsenic reduced from the root to the rice grains.

2.4. Assessment of Arsenic in Rice Plants by Pot Experiment

2.4.1. Experimental Condition for Pot Experiment

In the pot experiment, a portable greenhouse location was chosen at Kampung Hampar Beseri Perlis, Malaysia. During the day, the research area was designed on the basis of good exposure to sunlight. Because the experiment was performed in a greenhouse, the environmental conditions were constant. The portable greenhouse was used to shield the experiment from natural calamities (such as extreme drought and a northwest wind) as well as animal disruptions.

2.4.2. Soil Collection and Pot Preparation

Local paddy soil was collected from the paddy field located at Kampung Beseri Dalam, Perlis, Malaysia. Each soil sample was taken approximately at a depth of 0–15 cm using a hoe. Next, the soil was dried naturally under sunlight for three days from 8 am–5 pm. Subsequently, the soil ground was loosened by a gentle crushing using a rubber hammer and this process was continued with a used garden riddle soil sieve mesh (6 mm). At this stage, all debris plants such as roots, grasses and small stones were removed. About 8 kg of soil was then filled into a small basin container (0.05 m^2) in total with 27 pots comprising four different arsenic treatments (0, 2, 7, 12 mg/kg dry weight of arsenic) including one control plant with three replications. The physicochemical properties of soils used for the pot experiments were recorded as in Table 1.

Table 1. Physio-chemical properties of experimental pot.

Soil Parameters (%)	Range Condition
Clay	66–69
Sand	9–16
Silt	17–24
Texture	Clay foam
pH	7.7 ± 0.2

2.4.3. Rice Seedling and Cultivation

In this analysis, the MR220CL2 variety was used as a source for rice as it is widely grown in Perlis paddy fields. This variety was supplied by the Muda Agricultural Development Authority (MADA), Kangar. The period of maturity of this variety is about 120 days or equal to four months after seedling. The rice variety was immersed initially in a water bowl for one day. Immersed rice seeds were taken, and floating seeds were discarded. After this, tissue was used to remove the excess water from the rice seeds. All rice seeds were then ready for transfer to the pots.

2.4.4. Pot Experiment

The pot experiment was conducted to determine arsenic toxicity limits and symptoms in the rice plant. In each pot, 8 kg of the soil sample (in triplicates) was placed with two rice seeds (MR220CL2) and sown. The standard doses of N, P, K fertilizers together with different levels of arsenic (0, 2, 7, and 12 mg kg^{-1}) and control plants in a pentavalent pattern were applied to the pots after 12 days of sowing. The arsenic was applied in the form of sodium arsenate (Na_2HAsO_4), which can easily convert arsenic to arsenite under the reducing and submerged conditions of paddy soil [9]. Chemical fertilizers or nutritional solutions were not added to the pot soil. The soils in the pots were monitored and irrigated with arsenic-free water and maintained at field capacity. Therefore, there was no chance of arsenic input from the tap water to the pot soil. After the application of arsenic, soils were left in the pots for two days without irrigation. Tap water was then used to irrigate the pots in order to make the soil clay suitable for rice seedling transplantation. About 3–4 cm of water level above the soil surface was maintained in the pots before and after seedling transplantations. The water level was maintained in each pot throughout the growth period. Together with the first fertilizer, 1 mg kg^{-1} of silica nanoparticles and graphene was allocated for each pot in different levels of arsenic (in triplicates). Both nanomaterials we produced and utilized from the rice straw are illustrated in Figure 1b,c. The experiments were conducted using three different sets under similar conditions and parameters in order to reduce space and save resources. Three set of experiments were run for 360 days (120, 120, 120) respectively. After 25 days, urea fertilizer was applied to all the pots and the last fertilizer was applied at 70 days with the standard doses of N, P, K. All data measurements regarding plant growth were first measured on day 25. All experiments were conducted under netting area to avoid pest disturbing to the growth of the plant. The matured paddy growth was ready to harvest after 100 days, and irrigation was stopped before 10 days of harvest [22].

2.4.5. Analysis of Rice Grains Digests from the Pot Experiments

All the samples (grains) of matured paddy were collected and labelled in a sealed plastic container. Before digesting, the samples were stored in a chiller and kept under −20 °C to avoid drying. The extractions of grains were carried out by the wet method as described (AOAC 1984) [22]. Approximately 1.3–1.5 g of the extracted sections was weighed and placed in a conical flask and then supplemented with 15 mL of 69% concentrated nitric acid. The mixture of acid and plant samples was heated on a sand steam at a temperature of 90–100 °C until all nitric acid fumes had evaporated. Subsequently, 5 mL of 60% of the chlorophyll was added and the heating of the sample was continued until the yellow color was visible. After the sample was cooled to room temperature, the solution was filtered through a filter paper (Whatman No. 6) into a conical incision. The solution was then filtered again using filter paper (45 µm) and transferred into a 100 mL drug bottle. The resulting filtration was diluted to 50 mL with distillation and heavy-metal analysis was performed using Perkin ElmerElan 900 model Induction-Induction Plasma-Spectroscopy (ICP-MS). For each sample, three replicates were taken, and the mean values were calculated. The percentage of removal of arsenic was estimated from the initial and final concentrations using the following equation

$$\text{Percentages of Heavy Metal Removal} = (Ci - Cf)/Cf$$

where Ci = initial metal concentration in mg/L and Cf = final metal concentration in mg/L.

3. Results and Discussion

3.1. Screening Study for Arsenic Toxicity in Selected Area Paddy Plantation

In this study, the screening was purposed to determine the current situation on the availability of arsenic levels in paddy fields. In Malaysia, the Perlis states are well known for rice cultivation and rice granaries. Based on the results as shown on Table 2, the highest amount of arsenic was recorded in sample 2 with 3.07 mg/kg. This area is mainly located near residential houses, schools, administration offices and workshops. Thus, the high value of arsenic in this paddy field occurs due to the source of water-flow and its being used for irrigation. Apart from this, with the samples from other places, the average concentration was recorded in the range of 0.49 to 0.63 mg/kg. The low concentration of arsenic was obtained from this analysis due to this area being under observation by the local government as an agricultural site with no others outsource factors that contribute to increase the availability of arsenic in the area from muck, slag, and pit wastewater. However, based on this screening study from the selected area of the paddy field, the value obtained exceeds the permissible limit and is not safe for feeding purposes as proposed by the WHO. This received result also motivated us to work on safe limits of arsenic in rice grains.

Table 2. Screening study on available arsenic in rice grains at selected Perlis paddy plantation locations.

No of Sample	Concentration of Arsenic (mg/kg)	Location
1	0.57	06°24′43.28″ N 100°11′33.83″ E
2	3.07	06°25′50.87″ N, 100°13′23.05″ E
3	0.54	06°33′19.59″ N, 100°14′37.40″ E
4	0.49	06°21′46.32″ N, 100°10′21.50″ E
5	0.52	06°23′27.13″ N, 100°08′55.60″ E
6	0.63	06°38′12.94″ N, 100°15′41.62″ E
7	0.53	06°38′50.83″ N, 100°14′44.83″ E
8	0.56	06°24′31.78″ N, 100°14′01.41″ E
9	0.56	06°28′03.76″ N, 100°17′35.23″ E

3.2. Mechanism Reaction of Silica Nanoparticles and Graphene to Inhibit Accumulation of Arsenic

Based on the earlier studies, the application of silica nanoparticles has been shown to reduce the concentration of arsenic in rice and to have a beneficial impact on plant growth, such as improving yields of rice grains. At the beginning of the reaction, both silica and arsenic in the soil were competing for similar productive soil mineral adsorption sites. However, based on other studies, arsenic is bound to be both an amorphous low-crystalline hydroxide and a well-crystalline hydroxide of the elemental Fe and Al [23]. It aims to define and monitor the bio-accessibility of arsenic either in the rhizosphere or in non-rhizosphere soils of the paddy plantation. Paddy is mostly planted in anoxic conditions with a waterlogged system [24]. Usually, arsenic is present as arsenic (iii) where this metalloid reaches through the roots by sharing the silica transport pathway. Based on the previous report, the addition of silica nanoparticles in paddy plants minimizes the availability of arsenic, especially in rice grains [25]. It is due to the competition of the same pathway between silica and arsenic (iii) where Fleck and his researcher reported that the presence of arsenious acid as silicic acid inhibits the arsenic accumulation in rice plants, as illustrated in Figure 1d [26]. On the other hand, as one of the carbon nanomaterials, graphene also has a significant effect on the production as a slow-release fertilizer not only used as a nano-carrier for the plant nutrient but also as a competitive inhibitor of the mitigating heavy metals such as arsenic in the paddy plant [27]. This is because graphene provides a wide specific area (2630 m^2/g) with sp2 hybridized carbons and is significantly suitable for adsorbent material for metalloids, such as arsenic [28]. Recently, two and three dimensions of the graphene sheet were used for different purposes, primarily as adsorbents.

3.3. Adsorption Dosage of Silica Nanoparticles/Graphene with Varies Arsenic Concentrations

In this study, the adsorption dosage of both nanomaterials is shown and it was tested based on a laboratory experiment before being used in a pot experiment. The adsorption of pollutants is one of the most common applications with silica nanoparticles and graphene where both materials have been extensively utilized to adsorb the heavy metals, emerging pollutants and dyes [2,3]. At present, quantification determination of arsenic (III) is proceeding by the spectrophotometric technique using UV-Vis. Along with the experiment, a colored complex of arsenic with a variamine blue base dye was prepared because the arsenic formed as colorless. The arsenic was then reacted with acidified potassium iodate to liberate iodine and turn to a violet color. The maximum absorption, λ max was recorded at 326 nm and this means the whole reaction using UV-Vis needed to standardize with this wavelength (Supplementary Material). Subsequently, for the effect of the adsorbate analysis on arsenic removal, both silica nanoparticles and graphene as adsorbent showed a similar pattern where we could see that the highest concentration limit on arsenic removal was at the amount 1 mg/mL. At the beginning, at 0.2–0.4 mg/mL for silica nanoparticles, the bar graph shows that the total arsenic removal is less than 30%. When increasing the concentration from 0.6 to 0.8 mg/mL the total arsenic removal was increased to ~70%. The upcoming concentration then shows ~87% of total arsenic removal. Afterwards, when additional concentrations of silica were added from 1.2 to 2 mg/mL, it seems that the total arsenic removal was static or that only a slight difference occurred. The same goes for the graphene nanomaterial, where a similar pattern of the graph could be observed and the highest adsorption process was located at 1 mg/mL concentration with ~81% of arsenic removal. Briefly, this phenomenon occurred depending on the adsorption site surface of the arsenic. At the beginning when a low adsorbent concentration from silica nanoparticles and graphene was applied to the arsenic, there was a large surface site for the absorption process. However, when both adsorbents increased the concentration, they then covered all surface sites toward the arsenic until the capacity of the adsorbent became saturated; no more surface sites were free and the exchange sites were filled, leading to less adsorption efficiency [29]. Adsorption is a process that is dependent on surface-based processes and the outcomes of surface energy measurements. This is because of the way that the adsorption process operates. The precise nature of the bonding is determined by the species that are involved, but the adsorption process can be broken down into three broad categories: physisorption (characterized by weak van der Waals forces), chemisorption (characterized by covalent bonding), and electrostatic attraction between the adsorbate and the adsorbent. The exact nature of the bonding is determined by the species that are involved. This is demonstrated through the capacity of the adsorbate and the adsorbent to interact with one another [30]. The adsorbent pattern and percentages removal of arsenic graph are shown in Figure 2a,b. It is interesting to note that the % of the removal of heavy metals is proportional to the initial and final concentration of absorbance and a similar trend was observed and a similar conclusion was made in the study by Guoming and researchers [31].

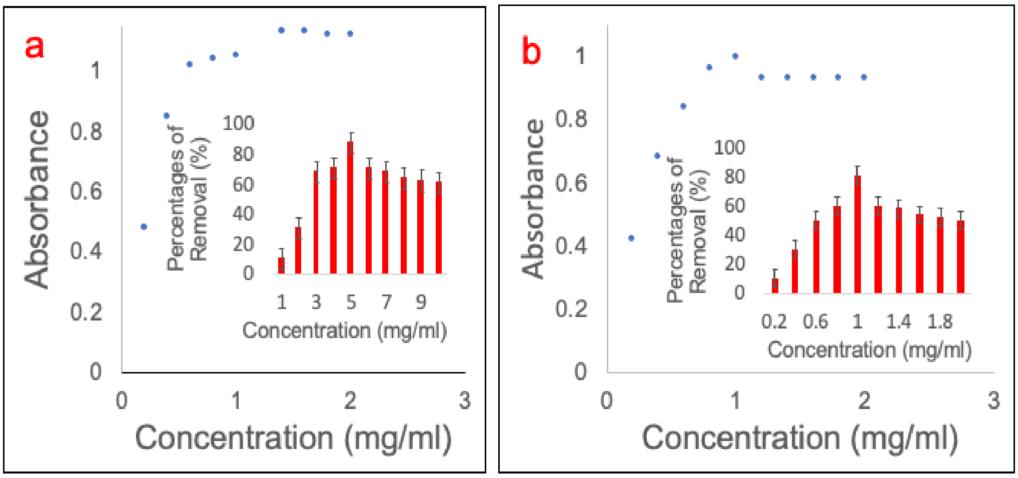


Figure 2. Adsorbent and percentage removal of arsenic for (**a**) Silica nanoparticles (**b**) Graphene. From the obtained results, the exact concentration for both nanomaterials were determined and used for pot experiment analysis.

3.4. Growth Parameters for Rice Plant in Pot Experiment

In the pot experiments, assessment of the arsenic toxicity and symptoms changed with each rice plant in a pot that was recorded. In this study, four-time intervals were used to record all changes that occurred along the growth of the paddy plant, on 25, 50, 75 and 100 days with the desired variety (MR 220CL2), ready to be harvested within 100 days. As mentioned in the early methodology under Section 2.4.4, various arsenic concentrations used in the pot experiment were selected as recommended by the European Community where the maximum acceptable limit is not more than 20 mg/kg [32,33]. During the experiment, both nanomaterials were tested at the same amount of 1 mg/kg and taken from the above result of the adsorption analysis, where both nanomaterials were applied to the fertilizer in order to study the effect of arsenic accumulation in rice grains. At the early growth stage, the number of active seedlings at the sowing and transplanting phase was grown similarly and noticed only on day 25, when the plant height was significantly reduced and was parallel with a high-dosage rate. With this, it could clearly be observed even at 25 days that the significant difference in plant height with the control plant was at the highest dosage of arsenic (12 mg/kg). Next, at the tillering and panicle initiation stage on day 50, we were able to observe the numbers of active tillers/plants develop with the different concentrations of arsenic applied. With the control plant (0 mg/mL), at least seven tillers were developed in each pot for both nanomaterials' treatments. Then, a reduction in tiller numbers clearly showed a significant effect of a high arsenic concentration, where at least four tillers (in silica) and five tillers (graphene) were observed at 12 mg/kg of arsenic concentration. Next, for the flowering stage around 75 days, we could observe a sudden death only with 12 mg/kg of graphene pots. This may be due to the toxic effect of the resulting plant growth and the fact that nanostructured materials can present toxicity. Interestingly, based on observation, the graphene restricted the growth of the paddy plant that died after 75 days; this could be the interference of graphene in slowing down the nutrient intake of the paddy plant. This equally confirmed the graphene's ability to restrict heavy metal intake by the paddy. Similar claims were found in the study of He [34]. Apart from this, based on previous studies, there are several impacts such as the inhibition rate of photosynthesis in plants causing disorganized functions of the plant growth even when graphene was applied. This is due to the limited active surface site for adsorbing excessive arsenic; hence, the paddy's growth could be disturbed [35,36]. Lastly, at the stage of maturity where ready to harvest, it could be observed that the control plant for both treatments with silica and graphene possessed a similar pattern in terms of plant height, to be 84.6 $\pm$ 3.0 and 82.7 $\pm$ 1.8 cm, respectively. However, it can be concluded that the trend in plant height followed a sequence, where lower concentrations showed higher rates of plant growth compared to the higher concentrations of arsenic used (0 > 2 > 5 > 7 mg/kg) as shown in Table 3.

Table 3. Data collection for plant height during nanomaterial treatment.

Nanomaterial	Arsenic Concentration (mg/mL)	25 days	50 days	75 days	100 days
Silica	0	51.3 ± 1.9	65.3 ± 2.0	70.3 ± 1.45	84.6 ± 3.0
	2	48.3 ± 3.3	65.0 ± 1.7	68.0 ± 1.7	78.7 ± 1.5
	7	40.3 ± 1.5	58.0 ± 1.7	65.7 ± 1.8	71.3 ± 1.9
	12	34.3 ± 1.2	54.3 ± 2.7	62.7 ± 2.3	68.0 ± 1.7
Graphene	0	46 ± 3.6	61.7 ± 2.0	79 ± 2.6	88.7 ± 1.8
	2	48.3 ± 2.6	58.3 ± 1.8	75.0 ± 3.8	81 ± 2.1
	7	41.0 ± 4.7	48.3 ± 1.8	58 ± 3.3	61 ± 4.1
	12	33.7 ± 2.3	39.7 ± 4.6	-	-

Furthermore, the number and weight of grains produced were reduced with increasing arsenic concentrations. As we can see in the control plant with only silica and graphene, it showed the highest number of grains compared with other concentrations. This means that the high concentration of arsenic also affects the number of grains and quality and weight of grains produced, as shown in Table 4.

Table 4. Data collection for tiller number, number of grains and weight grains in pot experiment.

Nanomaterial	Arsenic Concentration (mg/mL)	Tiller Number	Number of Grains	Weight of Grains (g)
Silica	0	8	728	20
	2	8	456	16
	7	6	348	12
	12	5	178	10
Graphene	0	8	735	19
	2	7	313	14
	7	5	309	11
	12	5	-	-

3.5. Symptoms Visualization of Rice Plant in Pot Experiments

Several graded doses of arsenic applied in the pot experiment led us to visualize the symptoms in the whole of the plant parts, such as the leaf and panicle being discolored with the changes in the rice plant. At the beginning of the sowing and transplanting phases, we can see that all seeds were maintained in the same environment and the seeds could grow well without any obvious effect. After 30 days, the panicle started to grow, and it was shown that the highest concentration of arsenic (12 mg/mL) disturbs the growth on the panicle for both treatments with silica nanoparticles (Figure 3a (i–iii)) and graphene (Figure 3b (i–iii)), where a small number of panicles was produced as compared with other concentrations (2 and 7 mg/kg). As compared to the control treatment in a pot experiment for silica nanoparticles and graphene (Figure 3c,d), both have shown a high number of panicles produced. It was proven that even a small dosage of arsenic produces an impact on the development of panicles in the plant. Based on the previous report, it was found that higher-level arsenic accumulation in the pot experiment affected the plant growth, where it caused the plant to become stunted and a small number of tillers and panicles was produced. Moreover, the symptoms were caused by acute chlorotic, where it affected the number and weight of grains produced [37,38]. As shown in (Figure 3e–g), after 70 days we could observe the visual symptoms that occurred on the leaf at concentrations of arsenic from 2, 7 and 12 mg/kg; visual symptoms were visible upon drying up as well as changes in the physiological growth of the plant such as exhibiting initial symptoms of leaf sheath and making the stem easier for lodging except for the plant treated without arsenic (Figure 3e(iv),f(iv)). Treatment with silica can sustain the growth until 12 mg/kg of arsenic is applied, but not with the graphene. For instance, as displayed in Figure 3f(i), the plant cannot sustain and survive for growth at 12 mg/kg of arsenic in graphene treatment and the whole plant is gradually dried up totally at harvest time. Furthermore, as compared with the control plant, we could observe plant growth without any disturbance until harvesting (Figure 3g).

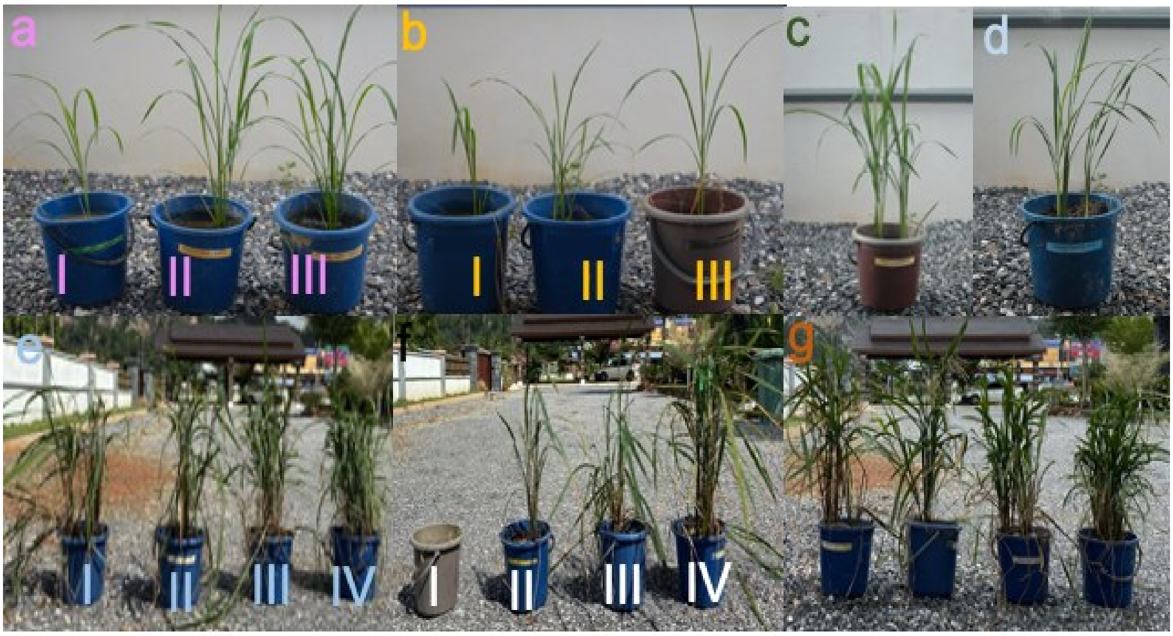
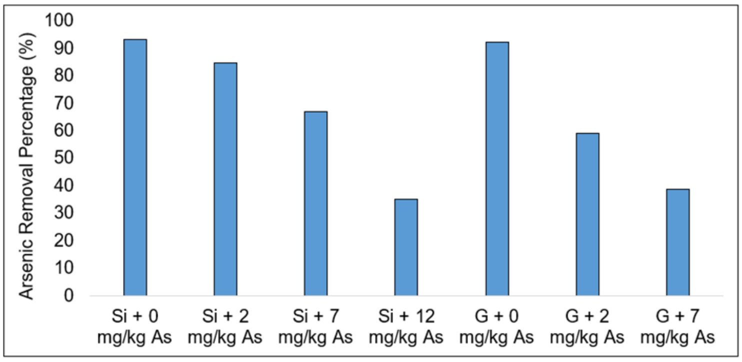


Figure 3. Visual observation. It is important to study the correlation impact on treatment and concentrations of arsenic applied and observe the growth parameter such as plant height. The symptoms were captured after 30 days at stage of tillering and panicle initiation between (**a**) silica nanoparticle (i) 12 mg/kg (ii) 7 mg/kg (iii) 2 mg/kg and (**b**) graphene (i) 12 mg/kg (ii) 7 mg/kg (iii) 2 mg/kg. Control plant for (**c**) Silica nanoparticles (**d**) Graphene. The visual was captured at day 70, flowering phases for (**e**) Silica nano particles (i) 12 mg/kg (ii) 7 mg/kg (iii) 2 mg/kg (iv) 0 mg/kg (**f**) graphene (i) 12 mg/kg (ii) 7 mg/kg (iii) 2 mg/kg (iv) 0 mg/kg and control plant. The controlled experiment set-up was carried out with four different pots which were labeled (**g**) and colored yellowish brown, four samples were selected in order to observe the growth trend. It is interesting to note that all these controlled set-ups without silica or graphene show exactly similar growth characteristics; this confirmed the uniformity of the controlled parameters.

3.6. Analysis of Total Arsenic in Rice Grains by ICP-MS

The potential of silica nanoparticles and graphene as value-added fertilizers in reducing arsenic accumulation with rice grains were studied comprehensively by inductively coupled plasma mass spectrometry (ICP-MS) analysis. Based on the result, the matured rice plant treated with silica nanoparticles in the pot experiments shows a high level of reduction in accumulation of arsenic by rice grains as compared with the graphene treated, even though a small amount of both nanomaterials was used (1 mg/mL). As referred to in Figure 4a, at 0 mg/kg of arsenic, silica nanoparticle, and graphene are able to remove close to 93% of the total arsenic availability in the pot soil. When the dosage was increased to 2 mg/kg, we could observe that the silica was able to draw more compared to the graphene, which were ~85% and 59%, respectively. The same pattern was observed when the arsenic was increased to 7 mg/kg, and we noticed that almost half of the arsenic was removed by using silica as compared to graphene. However, for the last and highest concentration, only silica was able to sustain to remove arsenic accumulation from the paddy grains and succeeded with ~35% of total arsenic removal. Apart from this, the additional silica nanoparticles added in the experiment increased the silica concentration availability in the soil. In addition, both molecules competed with each other; however, silica nanoparticles alleviated the arsenic to be fully absorbed in the rice as an end product by lowering the accumulation of arsenic in the rice roots and shoots. Based on a previous report, using silica nanoparticles has been demonstrated to significantly boost expression of the OsABCC1 arsenic transporter gene in rice roots, which may have important implications for reducing arsenic uptake by rice plants. This transporter reduces arsenic uptake by rice seedlings from their soil by sequestering arsenic in the vacuole [39,40]. For graphene, even though this has been supported by plenty of research experiments carried out in the laboratory regarding mitigation of arsenic adsorption, little was performed directly to the pot experiment [41–44]. Therefore, this research can help other researches to proceed with the usage of graphene in real practical samples in the paddy field. Furthermore, the ICP-MS result additionally reveals other heavy metal elements such as cadmium (Cd), lead (Pb), copper (Cu) and zinc (Zn) (Figure 4b).

a



b

	As (mg/L)	Cd (mg/ml)	Pb (mg/ml)	Cu (mg/ml)	Zn (mg/ml)
Si + 0 mg/kg As	0.0438	0.51	0.85	0.91	2.67
Si + 2 mg/kg As	0.0967	0.38	0.66	0.64	2.26
Si + 7 mg/kg As	0.2112	0.5	0.72	0.82	1.72
Si + 12 mg/kg As	0.4142	0.26	0.64	0.69	1.67
G + 0 mg/kg As	0.0489	0.39	0.64	0.72	1.92
G + 2 mg/kg As	0.2613	0.29	0.59	0.81	1.86
G + 7 mg/kg As	0.3912	0.44	0.62	0.83	1.61
Control Plant	0.6375	0.67	0.66	1.04	2.16

Figure 4. Inductively coupled plasma mass spectrometry analysis. All sample grains in pot experiment were collected after 100 days and went through grain digestion before being tested. (**a**) Arsenic percentages removal for different treatments; (**b**) Heavy metal reveal from ICPMS. Metals noticed are cadmium, lead, copper and zinc.

Based on this data, it was revealed that a high level of arsenic will have an impact on the availability of zinc content in the soil. As shown in the information for graphene, when arsenic was added to each pot, the level of availability of zinc reduced as compared with the control plant. However, with additional silica nanoparticles, it seems that they help to prevent the element zinc from dropping drastically in the pot experiment. Moreover, even when no arsenic was added as in the control plant pot, silica nanoparticles were able to keep and even increase the quantity and availability of zinc. Based on a previous report, it can be seen that plants that grow with a low zinc concentration will affect the quality and produce low yield grains post-harvest [45].

4. Conclusions

Under controlled environment conditions, we used a pot experiment for both nanomaterials to have a significant impact on mitigating arsenic accumulation. Silica nanoparticles tend to be more effective as compared to graphene in terms of reducing arsenic accumulation. The research discovery from this study has potentials for developing cost-effective strategies in reducing possible human health risk from the consumption of arsenic-containing rice products.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su15032633/s1, Figure S1: Topography images were evaluated using FESEM. (a) silica nanoparticles (b) graphene. (c) Absorption curve for Arsenic (iii). The wavelength range was selected and used for adsorption analysis using UV-Vis measurement.; Figure S2: (a) In pot experiment analysis MR 220 CL2 was chosen as variety. This variety has maturity period for 100 days before ready for harvesting. Thus, the growth of this variety consists of four important phases which is sowing and transplanting (25 days), tillering and panicle initiation (50 days), Flowering (75 days) and Harvesting (100 days). In this analysis, plant height measurement was taken to determine the correlation between concentration of arsenic applied and treatment with (a) Silica Nanoparticles (b) Graphene.

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