Spectrophotometric Analysis Assay for the Measurement of Arsenic Using Nanocomposite of Silica and Graphene

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Abstract. According to media reports in today’s world, millions of people across the globe are suffering from arsenic (As) toxicity. Arsenic heavy metal occurs in different oxidative states in the environment and enters in the food chain through soil and water. In the agricultural field, irrigation with arsenic contaminated water has a higher level of arsenic contamination on the top soil, which may eventually affects the quality of crop production. The major crop like rice requires a considerable amount of water to complete its lifecycle. In Asian countries like Malaysia, Brunei, Indonesia, and Thailand, arsenic intake from rice diet is significantly higher, as rice plants have a special ability to take up arsenic from the soil and water used in irrigation. The transfer of arsenic from soil to plant systems is a serious issue that leads to considerable human exposure in a dangerous way. The applications of nanotechnology play a vital role in many research fields. And therefore, this research, employs the implementation of nanotechnology approach such as silica-graphene nanocomposite that could be able to minimize the Arsenic heavy metal contamination issues.

1. Introduction

Rice is an essential food of vast people in the world. There are number of studies done by researchers concerning rice, however, rice issues still exist [1]–[7]. Nowadays, arsenic (As) contamination raises public awareness and concern globally because its affects human health as it is carcinogenic. This metalloid occurs naturally in paddy plantation area and major cause is coming from the excessive use of pesticides, fertilizers and, anthropogenic activities which led to increased pollution of soil [8]. Arsenic contamination is much more affected in rice plant compared to others crop due to anaerobic conditions. This condition will make faster movement for arsenic accumulation in paddy plant. And excess of this contamination will affect the growth of paddy significantly, such as lowering the titter, reducing the straw weight, reducing the height of plant and reducing crop yield [9-10].

Therefore, to overcome this problems, potential application of nanotechnology becomes vital field for today's innovation. Currently, nanotechnology covers all major sectors such as energy, medical healthcare, nano systems, environment, food science and agriculture [11]–[16]. By applying nanomaterials such as silica nanoparticles and graphene, this research can minimize the accumulation of arsenic from paddy plant. A part from that, both have capability in agriculture in terms of plant
growth, plant disease resistance and high quality of yield due to the uniqueness of their size which suite nanoparticles size.

2. Material and method

2.1 Materials

Rice paddy straw was obtained from nearest rice mill, Perlis, Malaysia. Distilled water was used throughout the experiments. All chemicals were used as received without further purification.

2.2 Production of Silica Nanoparticles using paddy rice straw ash

The production for whole process as shown in figure 1. The paddy rice straw was washed and cleaned by distilled water to remove dirt and surfactant. It was dried naturally for 3 days under sun light. The washed rice straw obtained was designated as unleached rice straw. Then the cleaned rice straw was burned and ash was collected as main material for silica production. Roughly, 20g of ash was mixed together with 400 ml of 2.5 M of NaoH and continued with stirred at 100°C for 4 H. All mixed solution was filtered using Whatman filter paper. Then, the filtered solution was titrated slowly using 2 M of sulphuric acid and stopped until the solution reached at pH7. Subsequently, the stirring was continued for 18 h for adequate for equilibrium mixture. Afterward, it was stopped and waited until two separated layer gel was formed. This layer was separated using centrifugation process (6000 rpm, 5min) where pellet was was washed three time with ethanol and two times with water. The pellet was dried at 80°C for 30 min.

![Figure 1. Experimental Setup for Production of Silica Nanoparticles.](image)

2.3 Chemical synthesis process of Graphene from paddy straw

The chemical synthesis of graphene from ash paddy straw process is shown in Figure 2. Briefly, 3 gm of ash was mixed together with 12 gm of KOH using mortar and pestle. This mixture was compacted into white porcelain crucible. Next, all mixture undergoes annealing process where the top of porcelain crucible needs to close by using crucible cap. This sample was annealed at 700°C for 2 h in muffle furnace. At this stage, KOH act to active the treatment of mixture. This mixture was stirred continuously for 6 h. At last stage, the sample was washed using distilled water and filtered to remove any excess of KOH. The filtered sample was dried at 150°C for 24 h.
2.4 Preparation and Synthesis of Silica coated –graphene nanomaterial

Briefly, 500 mg of silica with 2% APTES was mixed together and incubated for 1 hr. Next the process continued with centrifugation process where it was washed two times with distilled water. At this stage, Pellet was taken and combines with 500 mg of graphene in 1 ml distilled water. Both mixtures were incubated for 1 hr. Subsequently, the solution was centrifuged and pellet was taken and dried at 70 oC for 2h.

2.5 Spectrophotometric study of the interaction between arsenic and adsorption material

In this analysis, the prepared readily fine silica, graphene and silica -graphene was distributed in eppendorf tube where each tube was filled with 1mg for each material. Next, arsenic was filled (1mg) and mixture together with each material. This mixture was incubated for 30 min to 1 hr for equilibrium mixture. Lastly, all mixture was ready for measurement. The absorbance spectrum was recorded.

3. Result and Discussion

In this experiment, paddy straw has been selected for main resources for adsorption of arsenic analysis. This material is affordable and easy to find after harvested process in paddy field area because in Malaysia, rice plantation was covers about 600,000 ha of area, thus, utilization of this by product will lead to sustainability of environment. The by product is produced annually because in Malaysia most farmers plant paddy twice a year. Based on figure 3, the determination of range of arsenic by UV/Vis spectroscopy absorbance was recorded from 0-750 nm. The result shows that, 220 nm was suitable range for arsenic for the reactions where all the reaction with adsorption material will be conducted within this range. In this analysis, different range of concentrations of arsenic have been used, the graph shows a sequence pattern from high concentration (24m mg/ml) to lower concentration (0.75 mg/ml).
Figure 3. Scanning absorbance range for arsenic.

The spectrophotometric analysis assay continues with different material adsorption. Based on figure 4(a) silica nanoparticles has been used for this analysis. The particles size of this silica used in this analysis is measured 70nm where its consider as nanosized structure because nanomaterial only consider where the material is less than 100 nm [17]. The highest concentration give 0.35 O.D where the lowest concentration give 0.07 O.D. For figure 4(b), graphene has been used, the pattern shows similar as silica nanoparticles, however, the different only the result of absorbance where the highest absorbance located at 0.58 O.D and the lowest concentration located at 0.12 O.D. Lastly, the nanocomposite is consists of combination of silica nanoparticles and graphene. Based on this graph, its shows slightly high absorbance compared with the other graphs for high concentration 0.69 O.D and the lowest concentration is located at 0.1 O.D. This results clearly show that, nanocomposite play a tremendous properties because it has an offer for enhancement with their unique surface area and active sites for adsorption analysis [18].

Figure 4. Spectrophotometric Analysis of Arsenic with (a) Silica Nanoparticles (b) Graphene (c) Silica Graphene Nanocomposite.

A part from that, based on figure 5, the graph shows that, the percentages of arsenic removal with different adsorption material. Three adsorptions have been compared to evaluate which of the materials has the most sorption capacity. This result confirmed that, nanocomposite consist of silica nanoparticles and graphene shows a greatest effect of adsorption of arsenic at 24 mg/ml, this nanocomposite is capable to reach 51% of removing the arsenic, whereas for graphene it only indicates for 41% removal of arsenic. For silica nanoparticles even though it shown a lowest capacity adsorption but still it has proven that silica nanoparticles can be used as material for arsenic removal adsorption. A part that, the sizing of silica nanoparticles plays vital impact for sorption capacity where the smallest the particles will have a
big tendency of adsorption capacity. A study shown that if the material with less than 10nm being used for the reaction it will generates an electronic effect of the mechanism of the nanoparticles [19]

![Figure 5: Percentages of Arsenic Removal after Interaction with Nanomaterial](image)

4. Conclusion

Overall, silica nanoparticles, graphene, and nano composite silica graphene have facilitated a good adsorbent for arsenic removal using spectrophotometric analysis assay. Moreover, the synthesis and production of this nanomaterial is simple and be apple to penetrate and compete with other commercially adsorbent for arsenic.

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References

[1] M. N. A. Uda et al., “Immunosensor development for rice tungro bacilliform virus (RTBV) detection using antibody nano-gold conjugate,” AIP Conf. Proc., vol. 1808, no. October, 2017.
[2] M. N. A. Uda et al., “Reviewed Immunosensor Format Using Nanomaterial for Tungro Virus Detection,” vol. 832, no. November 2013, pp. 410–414, 2014.
[3] M. N. A. Uda et al., “Antimicrobial Activity of Plant Extracts from Aloe Vera, Citrus Hystrix, Sabah Snake Grass and Zingiber Officinale against Pyricularia Oryzae that causes Rice Blast Disease in Paddy Plants,” IOP Conf. Ser. Mater. Sci. Eng., vol. 318, no. 1, 2018.
[4] M. N. A. Uda et al., “Comparative Study Between Elisa And Surface Plasmon Resonance (Spr) For Rice Tungro Disease Detection,” vol. 9, no. 11, pp. 5568–5571, 2013.
[5] M. N. . Uda et al., A Disposable Biosensor Based on Antibody-Antigen Interaction for Tungro Disease Detection. Elsevier Inc., 2019.
[6] M. N. A. Uda et al., “Comparison Study of Two Different Isolation and Purification Method for Rice Tungro Bacilliform Virus (RTBV),” Agric. Agric. Sci. Procedia, vol. 2, no. August, pp. 107–112, 2014.
[7] M. N. A. Uda et al., “Immunosensor development formatting for tungro disease detection using nano-gold antibody particles application,” AIP Conf. Proc., vol. 1808, no. 020057, 2017.
[8] L. J. Looi, Z. A. Ahmad, W. Y. Lim, and H. Hazzeman, “Bioconcentration and Translocation Efficiency of Metals in Paddy (Oryza sativa);,” Sains Malaysiana, vol. 43, no. 4, pp. 521–528, 2014.
[9] M. T. Bhadha, J. H.; Vanweelden, “Arsenic Accumulation in Rice (Oryza sativa): An Overview,” Int. J. Environ. e Agric. Res., vol. 2, no. 4, pp. 72–75, 2016.
[10] A. Mitra, S. Chatterjee, R. Moogouei, and D. Gupta, “Arsenic Accumulation in Rice and
Probable Mitigation Approaches: A Review,” *Agronomy*, vol. 7, no. 4, p. 67, 2017.

[11] S. C. B. Gopinath, S. Ramanathan, K. Hann Suk, M. Ee Foo, P. Anbu, and M. N. A. Uda, “Engineered nanostructures to carry the biological ligands,” *MATEC Web Conf.*, vol. 150, p. 06002, 2018.

[12] M. A. M. Akhir *et al.*, “Ethylene Gas Sensing Properties of Tin Oxide Nanowires Synthesized via CVD Method,” *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 318, no. 1, 2018.

[13] N. A. Parmin *et al.*, “Voltammetric determination of human papillomavirus 16 DNA by using interdigitated electrodes modified with titanium dioxide nanoparticles,” *Microchim. Acta*, vol. 186, no. 6, 2019.

[14] S. A. B. Ariffin, T. Adam, U. Hashim, S. Faridah Sfaridah, I. Zamri, and M. N. A. Uda, “Plant Diseases Detection Using Nanowire as Biosensor Transducer,” *Adv. Mater. Res.*, vol. 832, pp. 113–117, 2013.

[15] T. Adam and U. Hashim, “Label Free Detection of Single Biomolecules,” in *2014 Fifth International Conference on Intelligent Systems, Modelling and Simulation*, 2014, pp. 1–8.

[16] T. Adam and U. Hashim, “Fabrication of Micro-Mixer for Life Sciences Applications,” 2014.

[17] M. E. Foo *et al.*, “Antimicrobial activity of functionalized single-walled carbon nanotube with herbal extract of Hempedu bumi,” *Surf. Interface Anal.*, vol. 50, no. 3, pp. 354–361, 2018.

[18] M. Habuda-Stanić and M. Nujić, “Arsenic removal by nanoparticles: a review,” *Environ. Sci. Pollut. Res.*, vol. 22, no. 11, pp. 8094–8123, 2015.

[19] M. Umadevi, T. Rani, T. Balakrishnan, and R. Ramanibai, “Antimicrobial Activity of Silver Nanoparticles Prepared Under an Ultrasonic Field,” *Int. J. Pharm. Sci. Naotechnology*, vol. 4, no. 3, pp. 1491–1496, 2011.