Remediation of arsenic-contaminated soil by chelating agents in shallot plantation land in Bima, West Nusa Tenggara

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Abstract. Arsenic (As) contaminated agricultural land in Bima is due to the use of synthetic fertilizers and excessive pesticides in the shallot cultivation system. One of the efforts to remediate the contaminated soil by using the chelating agent. The research aims to study the ability of various chelating agents to remediate As contaminated soil and also examined the effect of chelating agents on arsenic concentration in shallot bulbs and production. The study was conducted at the shallot production center of Kalampa Village, Woha Subdistrict, Bima Regency, West Nusa Tenggara, which indicated As contamination. The experiment used a randomized block design with three replication and five chelating agents i.e. biochar-compost, chitosan, EDTA, ammonium thiosulfate, zeolite, and control. All treatment of chelating agents can reduce As in the soil up to 70% and significantly different with control. Arsenic content in shallot bulbs with chelating agents treatment is within the safe limit (<1 mg kg⁻¹). Biochar-compost significantly increased the shallot yield. Meanwhile, EDTA treatment did not support shallot production. Biochar-compost and zeolite are recommended for application due to their ability to remediate arsenic in the soil, the lowest concentration of arsenic in shallot bulbs, and the ability to support optimal shallot production.

1. Introduction

Bima Regency is one of the production centers for horticultural crops in Indonesia, especially shallot production. In 2014, the plantation area of shallots was 13,795 ha, with a total production of 1,624,012 t [1]. Pests and plant diseases are the main obstacles in the cultivation of shallot plants in Bima. To prevent this, farmers tend to use pesticides intensively [2]. The production of shallots in Bima has increased every year, so the use of agrochemicals cannot be avoided.

Excessive use of agrochemicals, such as urea, phosphate, and pesticides to increase shallot production, causes a decrease in the quality of the soil and the environment. Inorganic fertilizers and pesticides play a great role in agricultural growth, but the indiscriminate application will damage the quality of soil, water, and air. The main toxin elements of inorganic fertilizers are cadmium, chromium, lead, nitrate, arsenic, nickel, manganese, fluoride, etc. [3]. Agricultural land contaminated with arsenic can cause growth disturbances for plants and can also contaminate their products, so that if consumed by humans it can cause health problems [3–5].

Arsenic is a heavy metal that is carcinogenic in humans [6]. Therefore, the polluted agricultural land needs to be remediated immediately. Arsenic is an identified key contaminant for many decades that
occurs in a variety of minerals including Arsenopyrite (FeAsS), Realgar (As_{2}S_{3}), Orpiment (As_{2}S_{3}), Arsenolite (As_{4}O_{6}), native arsenic in ores of copper, lead, cobalt, nickel, zinc, silver, tin and also as nickel glance (NiAsS) or mispickel [7]. Arsenic in groundwater is divided into two forms, namely the reduced form formed under anaerobic conditions, often called arsenite. The other form is the oxidized form, which occurs under aerobic conditions, commonly referred to as arsenate [8]. The efforts to restore agricultural land carried out in this study were the use of chelating agents to reduce arsenic in the soil.

Chelating agents are organic and inorganic compounds capable of binding metal ions through the chelation process [9]. Several studies using chelating agents for mobilization and removal of potentially toxic metals from contaminated soil have been conducted. EDTA (Ethylene Diamine Tetra Acetic Acid) is the most efficient chelating agent for increasing the uptake of metals by plants but is less suitable for large-scale field applications due to the low biodegradability of the chemicals [10–12]. Previous studies have shown that the use of EDTA, zeolite, chitosan, compost, and ammonium thiosulfate decreased Pb concentrations in the soil [13]. Chelating agents such as EDTA, zeolite, biochar-compost, chitosan, and ammonium thiosulfate are also expected to remediate contaminated soil in agricultural land [9,13–17]. The research aims to study the ability of various chelating agents to remediate arsenic-contaminated soil in shallot plantation land in Bima Regency, West Nusa Tenggara. Furthermore, this study also examined the effect of chelating agents on arsenic concentration in shallot bulbs and production.

2. Materials and methods

2.1 Materials

In this study shallot seedlings grown from shallot bulbs of the BIMA variety and used five varieties of chelating agents, namely EDTA, zeolite, biochar-compost, chitosan, and ammonium thiosulfate as treatment, and control. Inorganic fertilizer such NPK compound and SP36 are also used in shallot cultivation. Other chemicals such as nitric acid, perchloric acid, and the arsenic standard solution used for arsenic analysis in the laboratory.

Chitosan used in this study was made from crab shells through the deacetylation process of chitin into chitosan with a deacetylation degree of 86.27% and a viscosity of 384.35 Cp. Biochar-compost is made with a ratio of biochar : compost (1 : 4 w/w). Biochar is made from corn cobs, which is the dominant agricultural waste on-site. The zeolite used in this study has a CEC value of 72.96 cmol(+) kg⁻¹, which is the highest CEC value in commercial zeolite.

2.2 Methods

The research was conducted in 2018 at the shallot production centers in Kalampa Village, Woha Subdistrict, Bima Regency, West Nusa Tenggara. This location indicated that arsenic was contaminated in high concentrations (26.71 mg kg⁻¹) based on the results of the preliminary survey. Analysis of soil properties and heavy metals concentration were carried out in the Indonesian Agricultural Environment Research Institute (IAERI) laboratory. The experiment used a Randomized Block Design with 6 treatments, there were biochar-compost, chitosan, EDTA, ammonium thiosulfate, and zeolite and one of untreated soil as a control, each of them replicated 3 times. The chelating agent dose was given based on the Langmuir calculation which has been calculated according to the area of land. The doses used are zeolite 391 kg ha⁻¹, chitosan 3,485 kg ha⁻¹, EDTA 1,845 kg ha⁻¹, biochar-compost 3,864 kg ha⁻¹ and ammonium thiosulfate 5,526 kg ha⁻¹.

Plot size and land spacing according to local farmers' land at the experimental location. All chelating agent treatments were applied during soil cultivation before planting shallot seedlings. Fertilization using NPK compound fertilizer at a dose of 500 kg ha⁻¹ and SP-36 fertilizer at a dose of 100-150 kg ha⁻². Shallots were harvested after 70 days. The tubers are dried to a moisture content of about 80%.
The parameters observed included the physical and chemical properties of the soil, the concentration of arsenic in the soil before the application of the chelating agent, 7 days after the application of the chelating agent, and after harvesting. The arsenic concentration in shallot bulbs, onion plant growth, and shallot yields was also observed. The determination of arsenic metal uses the wet ashing method [18]. Data analysis used descriptive analysis by presenting the result of research regarding the ability of each chelating agent in soil remediation. Statistical analyses were performed using SAS 9.1 for Windows (SAS Institute, Cary, NC, USA). Analysis of variance (ANOVA) was carried out independently for each measurement using t-test of the GLM (General Linear Model) procedure of SAS. The data are presented as the means and standard deviation (SD) of three replicates.

3. Results and discussion

3.1 Arsenic levels and soil properties

The earth's crust contains 1.8 mg kg\(^{-1}\) of arsenic which is derived from the soil parent material [19]. Based on the preliminary survey, the arsenic content in the research location in Kalampa Village, Woha District was 26.71 mg kg\(^{-1}\) (table 1). Meanwhile, the critical limit for arsenic in the soil is 1 to 20 mg kg\(^{-1}\) [20]. The high level of arsenic in the soil at that location is thought to be due to the high intensity of pesticide application. Agricultural activities, such as the use of fertilizers, pesticides, and irrigating water, could increase the arsenic content in the soil [21]. Farmers in Bima apply pesticides almost every day. The application of pesticides in Bima is more intensive than at the center of the shallot industry in Java, namely Brebes, which only sprays pesticides every 2 days. The dominant market pesticide used by farmers in the research location contains arsenic (As) between 0.0021 to 0.0190 ppm. The several types of pesticides that are thought to contain arsenic include insecticides, herbicides, fungicides, and algacide [22]. Arsenic is also contained in N, P, manure, compost, and lime approximately 2.2 to 120 mg kg\(^{-1}\), 2 to 1,200 mg kg\(^{-1}\), 3 to 25 mg kg\(^{-1}\), 0.1 to 25 mg kg\(^{-1}\) and 2 to 52 mg kg\(^{-1}\), respectively [23].

| Soil properties       | Method          | Value   | Criteria[18]     |
|-----------------------|-----------------|---------|------------------|
| Texture:              |                 |         |                  |
| Sand (%)              | Pipette         | 26      |                  |
| Silt (%)              |                 | 42      |                  |
| Clay (%)              |                 | 32      |                  |
| pH                    | H\(_2\)O (1:5/w:v) | 5.95    | Slightly acidic  |
| Organic carbon (%)    | Walkey and Black | 0.95    | Very low         |
| Total N (%)           | Kjeldahl        | 1.24    | Very high        |
| Available P (mg kg\(^{-1}\)) | Olsen       | 71.54   | Very high        |
| Available K (mg kg\(^{-1}\)) | Morgan Wolf  | 176.18  | Very high        |
| CEC (cmol\(^{+}\) kg\(^{-1}\)) | Titration    | 32.63   | High             |
| Total metal:          |                 |         |                  |
| Arsenic (mg kg\(^{-1}\)) | Wet ashing   | 26.71   |                  |

Soil characteristics in the study sites showed that soil texture was clay loam with a low level of organic-carbon content but the availability of macronutrients N, P, and K was very high and the CEC value was high (table 1). Soil characteristics such as pH, organic carbon, texture (clay), and soil temperature affect the adsorption of heavy metals in the soil [24]. Soil with a clay loam texture has medium clay content and includes a moderate soil texture so that the absorption of heavy metal ions is...
also moderate. Soil texture and mineral types have an important role in the mobility of metals in the soil. However, the arsenic concentration in the study site was high due to the intensive application of pesticides in shallot cultivation. High CEC values also increase the adsorption of heavy metals, including arsenic, by the soil. Soils with high CEC, high clay content, and humus have a high adsorption capacity of heavy metals [25]. While, the soil with a low level of clay (sandy soil), CEC, and organic carbon have less ability to absorb heavy metals [25–27].

3.2 Reduction of arsenic concentration in soil

The chelating agent can rapidly decrease the arsenic concentration in the soil. The results of measurements of arsenic concentration on the seventh day after chelating agent treatment showed that the arsenic concentration in the soil decreased by more than 50%, although in the control soil it also decreased by 28% (figure 1a). The percentage reduction of arsenic concentrations in the soil at 7 days after application with biochar-compost treatment > chitosan > ammonium thiosulfate > zeolite > EDTA. Until harvest time, the arsenic concentration in the soil steadily decreased in both the treated and control soils. The results of measurements of arsenic concentration at harvest showed that the arsenic concentration decreased by more than 70% in the soil treated with chelating agents and 50% in the control soil. This is due to the soil characteristic in the research location has moderate clay content. Generally, soils having higher amounts of clay have high sorption capacity, and clay has a small pore size so they can absorb heavy metals [25,26]. At harvest time, the ability to reduce the arsenic concentration in the soil by the five chelating agents was different from that of the previous time. at harvest time, ammonium thiosulfate had the best ability followed by EDTA, zeolite, chitosan, and biochar-compost. Ammonium thiosulfate showed the highest percentage reduction in As metal of 74.34%. Ammonium thiosulfate treatment can reduce arsenic concentration 23.47% higher than control.

![Figure 1](image.png)

**Figure 1.** Arsenic concentration in the soil decreased by chelating agent treatments (a). Arsenic concentration in the soil and shallot bulbs reduced by chelating agent treatments (b). Different letter notations showed significantly differences at $\alpha = 0.05$ (t-test).

Arsenic concentration in soil and shallot bulbs with chelating agent treatments was lower than control (figure 1b). A chelating agent has been shown to increase arsenic removal in the soil, so that it can be effectively used in the remediation of arsenic contaminated soil. The arsenic concentration in the soil treated with chelating agents was significantly different from control. The lowest arsenic content in shallot was obtained in the zeolite treatment followed by biochar-compost, EDTA, ammonium thiosulfate, and
the highest was measured in the chitosan treatment (figure 1b). Maximum limit of arsenic contamination in shallot bulbs is 1 mg kg\(^{-1}\) [28]. The results of measuring the concentration of arsenic in shallot bulbs, both from treated and control plants, showed that the arsenic concentration was less than 1 mg kg\(^{-1}\). However, the arsenic content in shallot bulbs with chelating agent treatment was lower than the control. The low arsenic levels in shallot bulbs indicate a synergistic collaboration between the soil and chelating agents in preventing the absorption of arsenic metal by plants. Zeolite treatment gives the best performance to the arsenic concentration on shallot bulbs to 0.00 mg kg\(^{-1}\). Natural materials such as zeolites have been used to absorb heavy metals in the soil to reduce their availability to plants. Compared to other techniques, the use of zeolite is faster, cleaner, and cheaper [29]. Each chelating agent with specific properties gives different results on arsenic metal remediation in soil and plants.

Ammonium thiosulfate compounds act as chelating agents by increase the desorption of metals from the soil thereby increasing the bioavailability of metals in soil solutions, then metals available around the roots interfere with the absorption of nutrients needed by plants so the plant roots will reduce the metal by forming a reductase enzyme [13]. Chelating agent such as EDTA was the removal of metal contaminants, through the formation of soluble metal chelates [30]. EDTA has a better ability to move metal cations and only produce a little physical and chemical impact on the soil matrix. Furthermore, EDTA is a type of polycarboxylic amine acid, a complex of chelates containing certain metal cations such as Ca\(^{2+}\) and Mg\(^{2+}\), which able to form complexes with certain metals [13]. Zeolite, in general, are weakly acidic and sodium-form exchangers are selective for hydrogen, which leads to high pH values when the exchanger is equilibrated with relatively dilute electrolyte solutions, making metal hydroxide precipitation feasible [29]. Then, the previous study showed that natural zeolite can be used effectively for the removal of metal cations [29,31]. Chitosan has a demonstrated ability to bind transition metals, its metal-binding properties have attracted attention as a potential hazardous waste recovery material [32]. Biochar-compost with various ratios significantly reduced bioavailability of metals associated with pH change [15]. Biochar compost is a soil amendment agent as well as can be used as heavy metals adsorbent, the mechanism for arsenic removal by biochar is complexation and electrostatic interactions [33].

3.3 Shallot yield

The yield is indicated by the dry weight of the shallot (figure 2). The highest to the lowest production was biochar-compost, chitosan, zeolite, ammonium thiosulfate, and EDTA treatment. Biochar-compost treatment significantly increased production compared to control and other chelating agent treatments. Based on [34], the application of biochar compost has a positive impact on soil fertility through its effect on SOC, CEC, and available crop nutrition. Plant yields have increased significantly due to the availability of soil nutrients for plants with the addition of biochar-compost.

EDTA showed significantly lower yield compared to other treatments. It means that EDTA treatment does not support the production of shallot. The application of EDTA and ammonium thiosulfate on lead-contaminated soil in Brebes also inhibits the growth and production of shallots [13]. Biochar compost and zeolite are recommended for their ability to restore arsenic-contaminated soil, the lowest concentration of arsenic in shallot bulbs, and their ability to support an increased yield of shallots. Both are easy to find, making it easier for farmers in Bima to use. Based on Mahabadi et al. [35] when more zeolite was added to the soil, lower concentrations of Cd were detected in the leach solution. The preventive effect of heavy metals from leaching was found to be more pronounced when zeolite was applied to the clay.
Figure 2. The dry weight of shallot yields. Different letter notations showed significantly differences at $\alpha = 0.05$ (t-test).

4. Conclusions
The content of arsenic in Kalampa Village, Woha District, Bima Regency is 26.71 ppm. The chelating agent treatment was able to reduce arsenic in the soil ≥70%. Ammonium thiosulfate treatment reduced arsenic levels in the soil to 6.85 ppm with the highest percentage reduction in As levels, namely 74.34%. Arsenic content in shallot bulbs with chelating agent treatment is within the safe limit (<1 mg kg$^{-1}$). The application of chelating agents to the production of shallot plants showed that EDTA treatment did not support shallot production. Biochar-compost significantly increased the shallot yield. Biochar-compost and Zeolite are recommended for application because their ability to remediate arsenic in the soil is almost the same as EDTA and ammonium thiosulfate. In addition, zeolite and biochar-compost are also able to support optimal shallot production.

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References
[1] BPS-Badan Pusat Statistik Kabupaten Bima 2020 Kabupaten Bima dalam Angka 2020 (in Bahasa) Badan Pusat Statistik Kabupaten Bima Woha pp 117-124
[2] Setiani R, Mulyono D and Nurmalinda 2018 Strategi pengembangan bawang merah di Kabupaten Bima, Nusa Tenggara Barat (in Bahasa) Jurnal Ekonomi dan Pembangunan 26 2-3
[3] Rahman K A and Debnath S C 2015 Agrochemical use, environmental and health hazards in Bangladesh International Research Journal of Interdisciplinary and Multidisciplinary Studies 1(VI) 75-79
[4] Nonga H E, Mdegela R H, Lie E, Sandvik M and Skaare J J 2011 Assessment of farming practices and uses of agrochemicals in Lake Manyara Basin Tanzania Afr. J. Agric. Res. 6 2216-2230
[5] Adriyani R 2006 Control of environmental pollution caused by pesticide in agricultural process Journal of Environmental Health (JEH) 3 95-106
[6] Baars A J, Theelen R M C, Jansen P J C M, Hesse J M, van Apeldoorn M E, Meijerink M C M, Verdam L and Zeilmaker M J 2001 Re-evaluation of human-toxiological maximum permissible risk level RIVM Report Bilthoven 711701 025 The Netherlands
[7] Garba Z N, Gimba C E and Galadima A 2012 Arsenic contamination of domestic water from Northern Nigeria International Journal of Science and Technology (IJST) 21
[8] Istarani F and Pandebesie E S 2014 Study of the impact of arsenic (As) and cadmium (Cd) on decreasing environmental quality Journal of Engineering POMITS 3 2301-9271
[9] Aziz T, Amalia R P, dan Vishe D 2015 Removal logam berat dari tanah terkontaminasi dengan menggunakan chelating agent (EDTA) (in Bahasa) Jurnal Teknik Kimia 21 (2) 41-49p
[10] Tandy S, Bossart K, Mueller R, Ritschel J, Hauser L, Schulin R and Nowack B 2004 Extraction of heavy metals from soils using biodegradable chelating agents Enviro. Sci. Technol. 38 937-944
[11] Kos B and Lestan D 2004 Chelator induced phytoextraction and in situ soil washing of Cu Environmental Pollution Environmental Pollution 132 333-339
[12] Luo C L, Shen Z G and Li X D 2005 Enhanced phytoextraction of Cu, Pb, Zn and Cd with EDTA and EDDS Chemosphere 59 1-11
[13] Purbalisa W, Paputri D M W, Wahyuni S and Ardiwinata A N 2019 Evaluation of chelating agents for remediation of lead contaminated soil in Brebes Central Java In AIP Conference Proceedings 2120 1 p.040015 AIP Publishing LLC.
[14] Lestan D, Luo C L and Li X D 2008 The use of chelating agents in the remediation of metal-contaminated soils: a review Environmental pollution 153 3-13
[15] Liang J, Yang Z, Tang L, Zeng G, Yu M, Li X, and Luo Y 2017 Changes in heavy metal mobility and availability from contaminated wetland soil remediated with combined biochar-compost Chemosphere 181 281-288
[16] Ullah A, Ma Y, Li J, Tahir N and Hussain B 2020 Effective amendments on cadmium, arsenic, chromium and lead contaminated paddy soil for rice safety Agronomy 10 359
[17] He Y, Lin H, Jin X, Dong Y, and Luo 2020 Simultaneous reduction of arsenic and cadmium bioavailability in agriculture soil and their accumulation in Brassica chinensis L. by using minerals Ecotoxicology and Environmental Safety 198 1-9
[18] Eviati and Sulaeman 2012 Petunjuk teknis: Analisis kimia tanah, tanaman, air, dan pupuk (Edisi ke-2) (in Bahasa) (Balai Penelitian Tanah Bogor)
[19] Kabata-Pendias A 2010 Trace Elements in Soils and Plants CRC press New York 467
[20] Alloway B J 1995 Heavy Metal in Soils Blackie Academic and Professional Drodrecht p597
[21] Das H K, Mitra A K, Sengupta P K, Bossain A, Islam F and Rabbani G H 2004 Arsenic concentrations in rive, vegetables, and fish in Bangladesh: a preliminary study Environ. Int. 30 383–387
[22] Hooda P S 2010 Trace Elements in Soils Publication New Jersey p 595.
[23] Setyorini D, Soeparto and Sulaeman 2003 Konsentrasi logam berat dalam pupuk in: Prosiding seminar nasional peningkatan kualitas lingkungan dan produk pertanian (in Bahasa) (Pusat Penelitian Tanah dan Agroklimat Bogor) pp 219-229
[24] Zeng F, Ali S, Zhang H, Ouyang Y, Qiu B, Wu F and Zhang G 2011 The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants Environmental Pollution 159 84–91
[25] Alamgir M 2016 The effects of soil properties to the extent of soil contamination with metal Environmental Remediation Technologies for Metal-Contaminated Soils 1–19
[26] Gomes P C, Fontes M P, da Silva A G, de S Mendonça E and Netto A R 2001 Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils Soil Science Society of America Journal 65 1115-1121
[27] Basta N T, Pantone D J and Tabatabai M A 1993 Path analysis of heavy metal adsorption by soil Agronomy Journal 85 1054-1057
[28] Standar Nasional Indonesia 2009 *Standar Nasional Indonesia 7387: 2009 Batas maximum cemaran logam berat dalam pangan* (in Bahasa) (Badan Standarisasi Nasional Jakarta) pp 2-25

[29] Erdem E, Karapinar N and Donat R 2004 The removal of heavy metal cations by natural zeolites *Journal of Colloid and Interface Science* **280** (2) 309-14

[30] Vaxevanidou K, Papassiopi N and Paspaliaris I 2008 Removal of heavy metals and arsenic from contaminated soils using bioremediation and chelant extraction techniques *Chemosphere* **70** 1329-37

[31] Vrinceanu N O, Motelica D M, Dumitru M, Calciu I, Tanase V, and Preda M 2019 Assessment of using bentonite, dolomite, natural zeolite and manure for the immobilization of heavy metals in a contaminated soil: the Copşa Mica case study Romania *Catena* **176** 336-342

[32] Habibie S 2014 Chelation and metal-ion complex formation of chitosan treated cotton *Majalah Ilmiah Pengkajian Industri* **8** (3) 93-100

[33] Li H, Xiaoling D, Evandro B S, Letuzia M O, Yanshan Cand Lena Q M 2017 Mechanisms of metal sorption by biochars: Biochar characteristics and modifications *Chemosphere* **178** 466-478

[34] Agegnehu G, Bass A M, Nelson P N, Muirhead B, Wright G and Bird M I 2015 Biochar and biochar-compost as soil amendments: effects on peanut yield, soil properties and greenhouse gas emissions in tropical North Queensland, Australia *Agric. Ecosyst. Environ.* **213** 72-85

[35] Mahabadi A A, Hajabbasi M A, Khademi H and Kazemian H 2007 Soil cadmium stabilization using an Iranian natural zeolite *Geoderma* **137** 388-393