

APPLICABILITY OF FLY ASH, INTERMEDIATE MATERIAL, AND ZEOLITE FOR IMPROVING SOIL FERTILITY AND YIELD OF TWO IRANIAN RICE CULTIVARS GROWN IN CADMIUM-CONTAMINATED SOIL

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Abstract: Cadmium (Cd) as a highly toxic heavy metal can cause seriously harmful to human health. The present study aimed to investigate the effects of fly ash, intermediate materials, and zeolite on the yield performance of two cultivars of Iranian rice (Anbarbo and Champa) and the remediation of Cd-contaminated soil. The experiment was carried out in two crop years, 2019-2020 and 2020-2021, in both forms of field and pot cultivation. The research treatments included fly ash, intermediate materials, zeolite, and genotype. Plant variables were analyzed by a split-plot method as a randomized complete block design, and soil variables were analyzed by a random complete block method. Results showed that intermediate material was significantly associated with dry weight, biomass, root Cd content, stem Cd content, seed Cd content, and rice yield ($p < 0.01$). Genotype also significantly affected dry weight, biomass, root Cd content, and rice yield ($p < 0.01$), and the Champa variety had the highest yield. The field and pot experiment results showed that the intermediate material was significantly associated with the highest amount of dry weight and the lowest amount of root, stem, and seed Cd content. Fly ash significantly increased soil pH, cation exchange capacity, phosphorus, and reduced soil Cd content ($p < 0.01$). However, the highest amount of available soil potassium was observed in the zeolite treatment. The impact of zeolite on contaminated soil needs further exploration. In conclusion, this study suggested that one of the beneficial strategies to improve rice yield and the fertility of contaminated soils is using waste materials such as fly ash and its derivatives.

Keywords: Soil Fertility, Zeolite, Soil Chemical Properties, Plant Genotype, Dry Weight.

1. INTRODUCTION

Environmental pollution caused by industrial activities is widespread worldwide (Alvarez et al., 2015; Demir, 2022; Delangiz et al., 2022; Jelea & Baciu, 2023; Kavusi et al., 2023). Soils may become contaminated by the accumulation of heavy metals (HMs) via emissions from the rapidly expanding removal of high metal wastes, mine tailings, and industrial areas (Gerami et al., 2021; Shahi Khalaf Ansar et al., 2022). Each source of contamination has damaging effects on plants and animals; however,

metals such as arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), etc. in soils and water can present a serious concern due to their persistence in the environment (Zhang et al., 2018; Miletić et al., 2022). Therefore, one of the fundamental environmental challenges is the gradual increase in the concentration of HMs in the soil due to their non-degradation by microorganisms (Nobaharan et al., 2022). After absorption and accumulation in plant tissues, such metals pose severe risks to human health and other living organisms (Riotte et al., 2017; Hu et al., 2021; Carkaj et al., 2021; Bai et al., 2022). The growing trend

of the world's population and the gradual increase in environmental pollution have caused many problems, including the destruction of an essential part of agricultural soils. Therefore, the basic and serious challenges of the world in the next decade will be on the critical issue of food security from its quantitative and qualitative aspects (Sun et al., 2022). Moreover, pollutants such as Pb, Cd, and zinc are HMs in our regions; cleaning these toxic and dangerous metals from the environment and soil will be very important. (Amouei et al., 2012; Genc, 2021; Zuo et al., 2021; Kicińska et al., 2022). There are many physical and chemical methods for the treatment of soils contaminated with HMs, most of which, in addition to high costs, lead to the destruction of the physical and chemical structure and vital activities of the soil (Krämer, 2005; Damian et al., 2007). In-situ amendment technology has been widely used in natural soil management due to its simple operation and low cost (Yu et al., 2019; Damian et al., 2019). This technology has become a common trend in China to restore soil and improve fertility (Zhang et al., 2019). Recently, studies have been directed toward using waste and disposal materials to improve soil fertility and reduce the absorption of HMs in soil, and the use of the term passivation for this process has become standard (Yang et al., 2017a; Sanchez-Hernandez et al., 2019). Fly ash is an industrial solid waste material that produces 30 million tons annually, which has a deficient domestic demand and is mainly used in the production of bricks, road paving, and cement production in some countries (Xu & Shi, 2018; Bakare et al., 2019; Venkatesan et al., 2019). Fly ash is a byproduct of coal fuel, which includes silica, alumina, iron, and calcium oxides. There are C and F types of fly ash. The C type of fly ash has more than 10% of calcium oxide; it also has the property of cementation. Fly ash is extracted from the exhaust gases of coal-fired furnaces and non-plastic and fine silt, which is a different combination based on natural coal fuel, and fly ash is one of the waste materials in thermal power plants. India is the best place to produce fly ash due to raw materials and thermal power plants (Ahmaruzzaman, 2010).

Among the new solutions that have been used to increase the impact and prevent the loss of moisture and chemical fertilizers is the use of natural compounds such as zeolite minerals in agricultural fields (Polat et al., 2004). Zeolites are porous materials that act like molecular sieves with their crystal structure. Due to having open channels in their network, they allow the passage of some ions and block the passage of some other ions. Selective absorption and controlled release of nutrients by zeolite mean that if the type of zeolite used is correctly selected when added to the soil, it helps to improve plant growth by increasing the long-term

supply of moisture and nutrients. The research showed that the consumption of 9 tons of zeolite per hectare could increase the safflower seed harvest index by 5.07% compared to the treatment of not using zeolite, and its positive role in reducing the damage caused by water stress was proven (Lei et al., 2019). Some studies reported that the effect of different water stress levels and super absorbents' consumption on cell membrane stability was statistically significant. Therefore, the highest and lowest cell membrane instability, with an average of 82.09 and 80.63%, respectively, belonged to the irrigation treatment after 140 and 70 mm of evaporation from the class a pan (Siddiqui & Singh, 2005; Khadem et al., 2010; Yang et al., 2017b). The use of zeolite by providing more irrigation water to the roots creates better growth and development conditions for plants and reduces cell membrane destruction (Cochemé et al., 2003; Yin et al., 2017; Damian et al., 2018). Mirzakhani (2016) reported the effect of different levels of zeolite consumption on grain yield and plant biological traits, and the specific area of the flag leaf was significant. They also reported that 9 tons per hectare of zeolite consumption led to a 16.79% increase in yield compared to the control treatment. Siebielec et al., (2018) reported that the highest plant height, dry and wet weight, and thousand seed weight were observed in the zeolite treatment. El-Naggar et al., (2018) documented that applying zeolite under drought stress conditions significantly increased grain yield, number of grains per cob, and plant height. Even zeolite treatment led to the improvement of corn water consumption efficiency under stress conditions.

About 200,000 hectares of land in Khuzestan province have been dedicated to rice cultivation. Anbarbo rice and Champa rice are two local varieties of very high quality, aromatic, tasty, and completely natural Iranian products. Other rice varieties in this province are Tarem, Shamim, Sadr, and the local variety. Cadmium contamination is one of the significant issues in the agricultural sector, especially in rice fields, and its high accumulation in rice leads to a serious threat to public health. On the other hand, Khuzestan province is one of the important rice-growing areas in Iran, where soil pollution with HMs and other pollutants is high due to various industrial activities (Fouladi et al., 2021). The contamination of rice-cultivated soils in this province with elements such as Pb, Cd, nickel, and Cr has been reported (Fouladi et al., 2021; Hojati, 2019). Therefore, regarding the problem of Cd contamination in the paddy fields of this region and also the advantages of using fly ash, such as the cheapness, availability, and proven effectiveness, in this study, we investigated and evaluated 1) the effect and efficiency of fly ash and its derivatives, intermediate material, zeolite and genotype in improving the fertility

of polluted soils, 2) the effect and efficiency of fly ash and its derivatives, intermediate material, zeolite and genotype on yield performance in two forms of field and pot cultivation.

2. MATERIALS AND METHODS

2.1. Physico-chemical characterization of soil

The soil used in this study was taken from 0 to 30 cm depths in Safiabad, Dezful. Analysis of different physicochemical properties of field soil and pot soil was carried out in the laboratory.

The pH of the soil was calculated with a digital pH meter (Digison model D1-707) in a soil/water mixture at the ratio of 1: 2.5. The moisture percentage of the soil was calculated with a digital soil moisture tester (DM-15, Takemura, JAPAN). Available phosphorus in samples was detected using an Olsen method utilizing sodium bicarbonate as extracting agent (Singh et al., 2013). The nitrogen was detected by carrying an air-dried sample with 40 % NaOH and distillation pursued by titration with 0.1 M HCl using a KEL PLUS nitrogen estimation system (Classic DX, Pelican Equipment). The results are shown in Table 1.

2.2. Experimental site

This research was conducted on the fertility of soils contaminated with Cd and rice plant (*Oryza sativa L.*) in the Safi Abad-Dezful Agriculture and Natural Resources Research and Training Center in 2019-2021. This area is located northwest of Khuzestan province, with a longitude of 48 degrees and 32 minutes east, a latitude of 32 degrees and 22 minutes north, and a height of 82 meters above sea level, at a distance of 120 kilometers from the center of the province. In general, the climate of Khuzestan province is semi-tropical, with hot, dry, and long summers and rainy and humid winters. The hot season of Khuzestan starts in May and continues until the end of October. Rice is mainly cultivated in this province in the summer season, specifically in June or July, and the crop is harvested at the end of summer. The rainfall period is usually between November and May, and the amount of rainfall is higher in the northern regions of the Khuzestan Jalgal and less and more limited in the southern and eastern regions. The climatic conditions and water and soil characteristics of this province are prone to the growth of most agricultural plants, and the physiological adaptation of these plants to the climate of Khuzestan has made the dry matter accumulation of these plants very favorable and close to their genetic potential (Fouladi et al., 2021; Hojati, 2019). The sum of annual sunny hours is more than 2700 hours, and evaporation

(Class A pan) reaches more than 2400 mm. The annual precipitation in Khuzestan province is more than 350 mm. According to Köppen climate classification, this region is one of the semi-arid regions, and it has a warm climate.

2.3. Experimental Design

This experiment was done as a split-plot of a randomized complete block design in 3 replications during the two crop years of 2019-2020 and 2020-2021 in both field and pot cultivation. Research treatments included fly ash and its derivatives as the main factor in four levels of the control treatment (CK) (ordinary field soil contaminated with Cd without fly ash and its derivatives), fly ash (FA), intermediate materials (IP), and zeolite (ZE) and genotype as sub-treatment included two cultivars Champa (G1) and Amberbo (G2).

2.4. Preparation and characterization of treatments

Fly ash was readily available. In order to prepare the intermediate material (IP), first, fly ash was uniformly mixed with sodium hydroxide in the mass ratio of FA: NaOH = 5:6, and after cooling the resulting material, it was placed in an oven at a temperature of 200 degrees Celsius for 3 hours to crystallize. Then, after cooling, the crystallized materials were mixed with diluted hydrochloric acid with a concentration of 0.5 mM until its acidity reached neutral. Finally, it was dried at standard temperature and stored (Zhao et al., 2020).

In order to prepare zeolite (ZE), intermediate materials (IP) were mixed with hydrogen peroxide at a mass ratio (IP: H₂O₂) = 1:6 and placed in an oven with a temperature of 200 degrees Celsius for 24 hours to perform a hydrothermal reaction. After cooling, the resulting material was combined with diluted hydrochloric acid with a concentration of 0.5 mM, and finally, the zeolite composition was obtained. The resulting zeolite was dried at room temperature and stored (Zhao et al., 2020).

2.5. Pot soil contamination protocol

Contaminating the soil with Cd was done using Cd nitrate salt Cd(NO₃)₂.4H₂O by spraying the solution on all parts of the soil. After contamination, the soils were transferred to plastic bags without drains. In order to reach ion balance, they were kept in these bags for two weeks in a greenhouse at a temperature of 20° Celsius and relative humidity of 53% until the interaction between the pollutants and the soil was formed. To prepare the planting bed and the research treatments, some of this soil was set aside for the

Table 1- Physical and chemical characteristics of the soil of the study area

Depth (cm)	Sand %	Silt %	Clay %	Available potassium mg/kg	Available phosphorus mg/kg	Total N %	pH	EC ds.m ⁻¹
0-30	31	35	34	108	6.9	0.17	7.1	0.99

control treatment. Then the rest was divided into three parts, and the ratio was 5:1 (5 ratios of Cd-contaminated soil and one ratio of fly ash, intermediate materials, and zeolite) was mixed and transferred into the pots (Zhao et al., 2012; Zhao et al., 2020).

2.6. Field soil contamination protocol

Contamination of the rice cultivation bed in the field was done by irrigation with water contaminated with Cd. First, contaminated water was prepared in the irrigation water tank by adding 20 mg of Cd nitrate salt from the molar mass of Cd nitrate salt per liter. The soil of the test site was irrigated by flooding method with Cd-contaminated water to the field capacity for two weeks. Then the field soil was sampled, the amount of Cd was measured, and the seedlings were transferred to the field (Zhao et al., 2012; Zhao et al., 2020).

2.7. Pot experiment

First, before adding soil, the holes in the bottom of the pot were covered with pieces of stone, and 10 cm of coarse sand was poured on it as drainage. The pot dimensions were 50 x 50 cm in the pot experiment, and 16 plants were grown in each pot. Then, 5 kg of soil contaminated Cd, mixed with air ash compounds, intermediate material, and zeolite, and kept for seven days with the moisture of field capacity. In order to use essential fertilizer, 90 kg/ha of nitrogen from the source of urea (46% pure nitrogen), 50 kg/ha of phosphorus from the source of ammonium phosphate (46% of phosphorus), and 30 kg/ha of potassium from the source of potassium sulfate (50% of potassium) respectively were used. The amount of fertilizer for each pot was 7 g of nitrogen, 4 g of phosphorus, and 2.5 g of potassium. Irrigation and weeding operations were done by hand. According to the pot's size, the required soil volume, and desired soil properties, a certain amount was applied to the pot.

2.8. Field experiment

Plowing, disking, leveling, and demarcation of the studied field were done at the end of June. Before planting, soil sampling was done in a zigzag pattern from a depth of 0-30 cm to determine the physical and chemical properties of the soil. In order to prepare seedlings, paddy was planted in a transplant tray in the

rice seedling breeding place on June 15th, and then the seedlings were transferred to the mainland on July 10th. Seedlings were planted at 20x25 intervals in each plot. In the field experiment, the dimensions of the plot were 11x11 meters. Before transferring the seedlings to the mainland, NPK fertilizers were used in the ratio of 13:5:10. Also, during the tillering period, urea fertilizer at the rate of 120 kg/ha and potassium fertilizer at the rate of 120 kg/ha was applied.

2.9. Plant sampling

Sampling was done by simple random sampling in the physiological treatment stage. After the plants were fully cured, they were cut from one centimeter above the soil surface, washed with dilute hydrochloric acid (0.1 normal), and transferred to paper envelopes. They were dried, weighed, and separated into different tissues, then powdered with an electric mill to measure the amount of Cd during chemical tests. These plants were divided into six parts: root (R), stem (S), leaf (L), rice husk (RH), and rice grain (RG). The biomass of each sample plot was equal to the total dry weight of aerial parts and rice roots (Chen et al., 2019).

2.10. Data analysis

Data were statistically analyzed using SAS 9.4 software (SAS Inc.). Treatment effects were studied by analysis of variance ANOVA with Duncan's test at a probability (p) level of <0.05 at 95% interval confidence. Graphs were drawn using Excel 2013 software.

3. RESULTS

3.1. Effect of the reclamation treatments and genotype on rice yield in the field experiment

The results showed that rice yield was significantly different under the influence of intermediate materials treatment ($P \geq 0.01$) and genotype ($P \geq 0.01$), as well as the interaction effect of these two treatments ($P \geq 0.01$) (Table 2).

The highest yield was observed in the IP treatment at the rate of 3391.9 kg/ha, which was not statistically significantly different from the zeolite treatment. The lowest yield was observed in the control treatment at 3230.8 kg/ha (Figure 1). The highest yield

Table 2. Composite variance analysis of plant dry weight and measured yield of rice in the field

Source of variation (S.O.V)	Degree of freedom (df)	Mean square(MS)	
		Plant dry weight	yield
Year	1	0.02*	2574.5*
Year × Repetition	4	0.1**	1566.67 ^{ns}
Fly ash derivatives	3	2.03**	64284.44**
Year ×Fly ash derivatives	3	0.002 ^{ns}	526.81 ^{ns}
Error a	12	0.01	2881.4
Genotype	2	3.29**	1051109.64**
Year ×Genotype	2	0.0006**	1511.63 ^{ns}
Genotype ×Fly ash derivatives	6	0.002 ^{ns}	10722.64**
Year ×Genotype×Fly ash derivatives	6	0.0009 ^{ns}	684.67 ^{ns}
Total Error	48	0.004	726.14
CV	-	4.66	6.81

^{ns}, * and **, respectively, non-significant, significant at the probability level of 5 and 1 percent

was observed in the Champa variety (3476.7 kg/ha), and the lowest yield was observed in the Ambarbo variety (3180.7 kg/ha). So, the IP and zeolite treatments were significantly higher than the control and fly ash treatments (Figure 2).

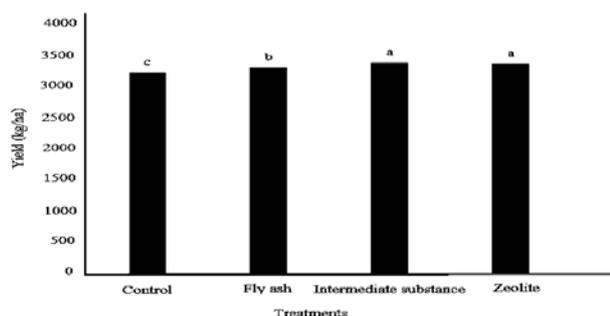


Figure 1. The effect of fly ash derivatives treatment on the yield of rice in field

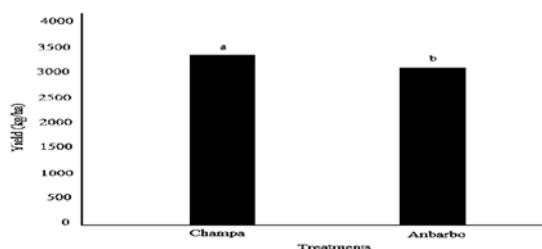


Figure 2. The effect of genotype treatment on rice yield in the field

In the experimental conditions, the yield of the Champa cultivar was 10% higher than that of the Ambarbo cultivar. The average yield of the Champa variety in Khuzestan is about 4.5-5 tons per hectare, and the average yield of the Ambarbo variety is about 3.5 tons per hectare (Limochi, 2013). Regarding the interaction effect of fly ash derivatives treatment and genotype, the highest yield was observed in intermediate material and Champa variety (3555.9 kg/ha), and the lowest yield was observed in the

control treatment and Ambarbo variety (3065.4 kg/ha) (Figure 3). Also, the yield of the Champa variety in the treatment of intermediate material is higher than that of fly ash.

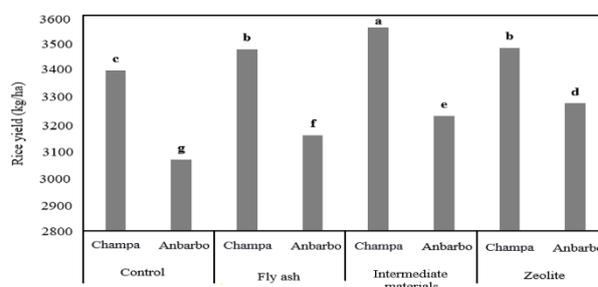


Figure 3. Interaction effect of treatment of fly ash derivatives and genotype on rice yield in the field

3.2. Effect of the reclamation treatments and genotype on rice yield in the pot experiment

The results showed that the effect of fly ash treatment and its derivatives on rice yield had a significant effect ($p < 0.01$). The effect of genotype also had a significant effect on rice yield ($p < 0.01$). According to the results, the interaction effect of fly ash treatment and genotype significantly affected rice yield ($p < 0.01$). Likewise, the main effect of year and the interaction effect of fly ash and genotype had no significant effect on dry weight and rice yield (Table 3).

The potted conditions result showed that the highest yield was observed in the IP treatment at 3505.4 kg/ha, which statistically had no significant difference from the zeolite treatment. The lowest yield was observed in the control treatment at 3333.5 kg/ha (Figure 4). In other words, the use of IP increased the yield of rice by 5%.

The highest yield was observed in the Champa variety (3585.8 kg/ha), and the lowest yield was

Table 3. Composite variance analysis of plant dry weight and measured yield of rice in the pots

Source of variation (S.O.V)	Degree of freedom (df)	(MS) Mean square	
		Plant dry weight	yield
Year	1	0.003 ^{ns}	114.91 ^{ns}
Year × Repetition	4	0.13 ^{**}	2733.68 ^{**}
Fly ash derivatives	3	1.97 ^{**}	69628.36 ^{**}
Year × Fly ash derivatives	3	0.001 ^{ns}	15.43 ^{ns}
Error a	12	0.006	904.67
Genotype	2	4.33 ^{**}	1031200.56 ^{**}
Year × Genotype	2	3.52 ^{**}	0.21 ^{ns}
Genotype × Fly ash derivatives	6	0.001 ^{ns}	9790.50 ^{**}
Year × Genotype × Fly ash derivatives	6	0.004 ^{ns}	10.68 ^{ns}
Total Error	48	0.003	504.19
CV	-	4.53	6.65

^{ns}, * and ^{**}, respectively, non-significant, significant at the probability level of 5 and 1 percent

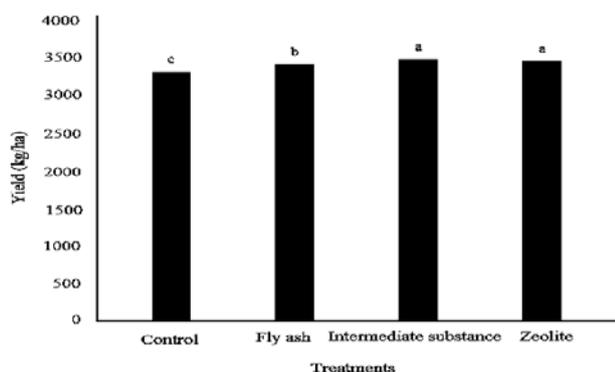


Figure 4. The effect of fly ash derivatives treatment on the yield of rice in pots

treatments of fly ash, IP, and ZE.

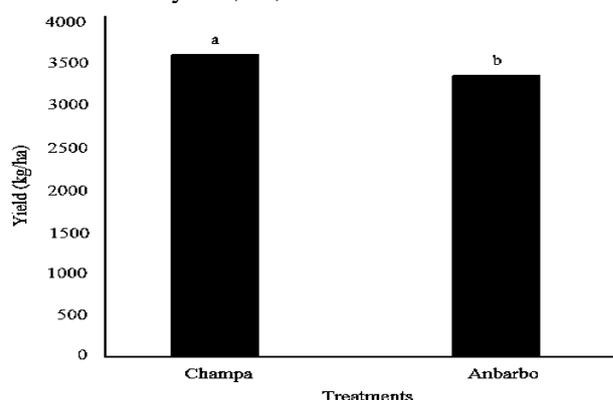


Figure 5. The effect of genotype treatment on rice yield in the pots

observed in the Ambarbo variety (3292.6 kg/ha) (Figure 5). In other words, the Champa cultivar yield was 9% higher than the Amberbo cultivar in the pot experiment conditions ($p < 0.05$).

The effects of IP and genotype interaction on rice yield showed that the highest yield was under IP and Champa cultivar (3668.1 kg/ha), and the lowest was under the control treatment and Amberbo cultivar (3162.5 kg/ha) (Figure 6) ($p < 0.05$). Even the yield of the Champa cultivar in the control treatment was higher than the yield of the Amberbo cultivar in all

3.3. Effect of the reclamation treatments and genotype on rice traits and Cd content

The results showed that the effect of IP on plant dry weight, biomass, root Cd, stem Cd, and seed Cd content had a significant effect ($p < 0.01$). Genotype also significantly affected dry weight, biomass, and root Cd content ($p < 0.01$), but it did not significantly affect Cd content in stem organs and rice seeds. The

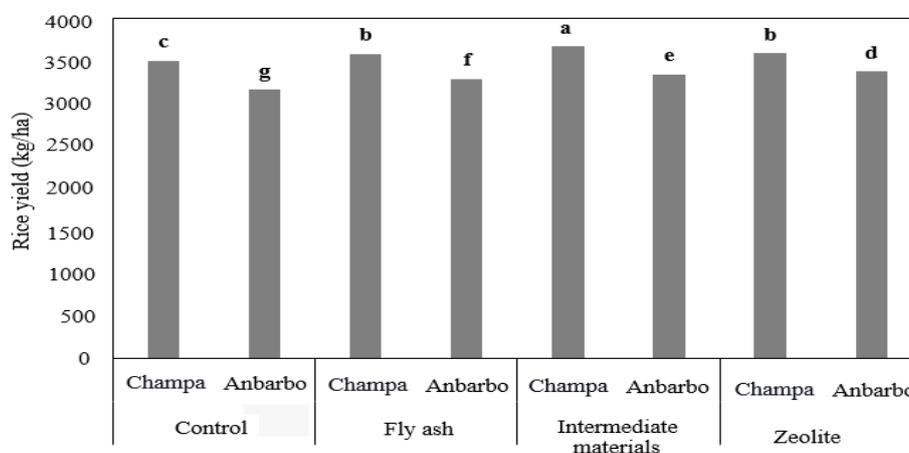


Figure 6. Interaction effect of treatment of fly ash derivatives and genotype on rice yield in the field

Table 4. Composite variance analysis of the measured data of field soil

Source of variation (S.O.V)	Degree of freedom (df)	(MS) Mean square				
		PH	Available potassium	CEC	soil phosphorus	Soil cadmium
Year	1	0.0006*	0.002 ^{ns}	0.005 ^{ns}	0.005 ^{ns}	0.000005**
Repetition	2	0.01**	0.01 ^{ns}	0.02 ^{ns}	0.51**	0.00001**
Fly ash derivatives	3	0.009**	0.47**	3.80**	2.18**	0.00008**
Total Error	23	0.0001	0.008	0.03	0.06	0.0000004
CV	-	0.21	1.81	1.44	1.79	0.91

^{ns}, * and ** respectively, non-significant, significant at the probability level of 5 and 1 percent

interaction effect of fly ash and genotype did not significantly affect the dry weight, biomass, and Cd content in rice's roots, stems, and seeds (Table 4).

3.4. Effect of the reclamation treatments and genotype on the dry weight and biomass

Results showed that dry weight was affected by fly ash ($P \geq 0.01$) and genotype ($P \geq 0.01$). The highest amount of dry weight was observed in the fly ash treatment (10.48 g), and the lowest amount of dry weight was observed in the control treatment (9.53 g) (Figure 7). As well the highest amount of dry weight was observed in the Ambarbo genotype (10.3 g), and the lowest amount was observed in the Champa genotype (9.74 g) (Figure 8).

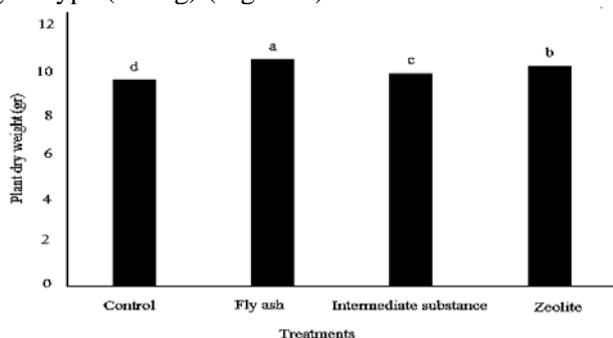


Figure 7. The effect of fly ash derivatives treatment on plant dry weight in the field

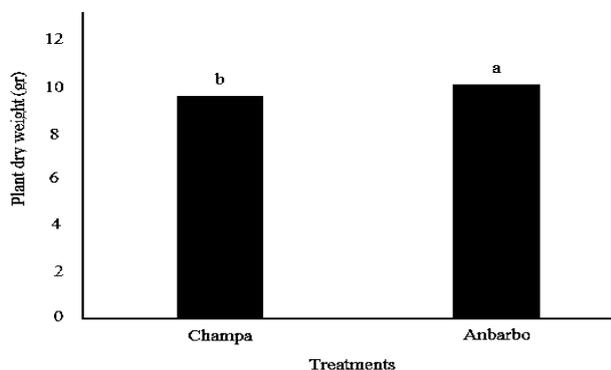


Figure 8. The effect of genotype treatment on plant dry weight in the field

The amount of biomass was significantly different under the influence of fly ash derivatives treatment ($P \geq 0.01$) and genotype ($P \geq 0.01$) (Table 4).

The highest amount of biomass was observed in the IP treatment (87.1 g), and the lowest amount was observed in the control treatment (80.5) (Figure 9). Furthermore, the highest amount of biomass was observed in the Ambarbo variety (84.86), and the lowest amount was observed in the Champa variety (83.38 g) (Figure 10).

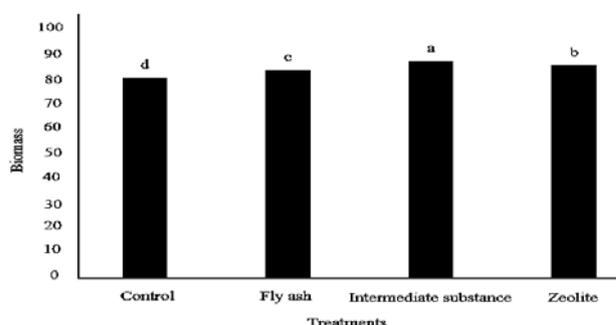


Figure 9. The effect of fly ash derivatives treatment on biomass in the field

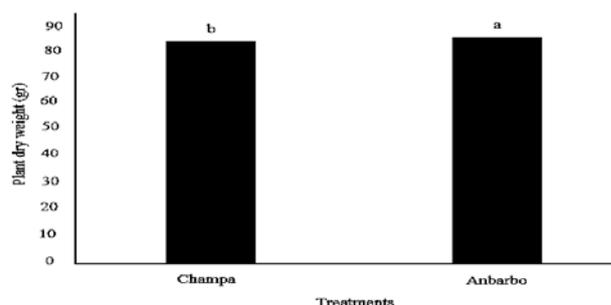


Figure 10. The effect of genotype treatment on biomass in the field

3.5. Distributions of Cd elements in rice

The highest amount of root Cd was observed in the control treatment (0.139 mg/kg), which, of course, was not significantly different from the amount in the intermediate treatment (0.133 mg/kg) and the lowest amount was in the fly ash treatment (0.112 mg/kg). Also, the highest amount of root Cd was observed in the Champa genotype (0.125 mg/kg), and the lowest amount was observed in the Ambarbo genotype (0.124 mg/kg). Moreover, the highest Cd content in the stem was observed in the control treatment (0.0947 mg/kg), and the lowest Cd content was in the fly ash treatment

(0.0735 mg/kg).

Furthermore, the highest amount of seed Cd was observed in the control treatment (0.116), and the lowest amount was in the fly ash treatment, (0.109).

3.6. Effect of the reclamation treatments on soil parameters

Since the genotype cannot affect the properties of the field soil, the genotype factor was removed from the analysis in this part, and the analysis was carried out in the form of a randomized complete block design in two years. The results significantly showed the effect of fly ash and its derivatives on soil pH, potassium bioavailability, cation exchange capacity, soil phosphorus, and Cd (Table 4). In this regard, there was a significant difference in soil pH under the influence of fly ash derivatives treatment ($P \geq 0.01$). And the highest pH was observed in the fly ash treatment (5.32), and the lowest was observed in the control treatment (5.23). Also, the results showed that there was a significant difference ($P \geq 0.01$) in the soil potassium bioavailability under the influence of fly ash derivatives treatment (Table 4). And the highest potassium bioavailability was observed in the zeolite treatment (5.32), and the lowest was observed in the control treatment (4.71). Based on the average comparison results, the highest amount of cation exchange capacity was observed in the fly ash treatment (12.33), and the lowest amount was observed in the control treatment (10.46).

The results also showed that the highest soil phosphorus was observed in the fly ash treatment (14.71 mg/kg), and the lowest amount was observed in the control treatment (13.37 mg/kg). Moreover, the highest soil Cd content was observed in the control treatment (0.077 mg/kg), and the lowest amount was observed in the fly ash treatment (0.069 mg/kg).

4. DISCUSSION

Fly ash and other derivatives have some chemical and physical properties that might be useful for soil remediation, i.e., improved soil quality (Ram & Mastro, 2014). Applying fly ash and its derivatives improves soil permeability and moisture holding capacity and reduces acidity and HMs availability (Pandey & Singh, 2012). The general characteristic of fly ash, zeolite, and other derivatives is to absorb and retain moisture in its texture; Therefore, by absorbing moisture, it provides this moisture to the plant over time and causes the plant to have moisture available throughout its growth period and the drought stress, which is one of the significant environmental stresses in hot and dry regions, does low affect the plant and the

plant structures are fully formed. Of course, soil water retained by the applied substances can only partially alleviate the drought stress because irrigation is the main measure to solve soil and plant water stress. Therefore, more biomass and dry matter are expected to be obtained. As well, the yield of the plant will increase compared to other treatments, and the findings of this study support these results. In agreement with our findings, Zhao et al., (2020) also reported that under Cd stress, the use of fly ash and its derivatives could improve the growth and yield characteristics of rice. They reported that intermediate materials and zeolite obtained from fly ash could increase the root length by 20.6%. Also, based on their findings, biomass increased by 26.3% under the influence of fly ash compared to the control treatment. They stated that the positive effect of fly ash and its derivatives in Cd-contaminated soils could be due to the soil's high silica content, which leads to the growth and development of rice plant structure. These findings are in agreement with the research of Balakhnina et al., (2015).

Lim et al., (2016) also reported that silica supplementation led to a successful reduction of Cd contamination and improved growth, which is similar to the findings of this research. Other research also confirmed that silica is a valuable element for plants and has a positive and significant effect on promoting crop growth and yield (Yu et al., 2019). Huang et al., (2020) and Yong-Chun et al., (2015) reported that the reason for increased yield in the presence of fly ash is the increase in the silica content of the soil, which leads to an increase in the absorption and efficiency of the use of nutrients by plants, and also with sedimentation. Silica in plant tissues and the formation of silica crystals increases the plant's resistance to the stress caused by Cd pollution. It causes Cd cannot accumulate in plant tissues and also causes an increase in biomass (Balakhnina et al., 2015). It could also be said that less biomass production in the control treatment may be due to the poisoning caused by the absorption of Cd by the plant, which inhibits the plant's growth and can lead to a decrease in biomass and plant performance. Some studies showed the positive effect of fly ash on indicators such as biomass, dry weight, and plant yield due to the release of essential elements such as silica and aluminum, etc. in the soil (Huang et al., 2020). Some studies reported that the creation of Cd ionic bond with fly ash, intermediate materials, and zeolite leads to the stabilization of Cd and its non-absorption by the plant; therefore, the absorption of soil nutrients by the plant is improved, and soil fertility increases. In agreement with the findings of this research, Shaheen & Rinklebe (2015) reported that fly ash is a low-cost method to increase rapeseed biomass and also reduces the exchangeable soluble Cd in the

soil by 4-60%. They stated that zeolite is more economical to reduce Cd pollution and increase activated carbon by 31-36%. Although, some researchers reported that fly ash could lead to secondary pollution in addition to the mentioned advantages. Chaudhary & Ghosh (2013) reported that applying fly ash can induce growth in *Jatropha* (*Jatropha curcas*), but it may reduce soil nutrients at higher levels. On the other hand, the cost of producing synthetic zeolite from fly ash is high, which is not cost-effective on a large scale to improve the pollution caused by Cd.

The amount of Cd in the organs of the rice plant under the influence of fly ash and its derivatives treatments had a significant difference compared to the control treatment and was lower. Analysis of two-year data showed that the concentration of Cd in rice organs is higher in the root, leaf, rice husk, and rice grain, respectively. The main reason for this phenomenon is that the roots first do Cd absorption. It is transferred to other tissues during the active transfer and diffusion process. Then it penetrates and precipitates in them, a completely irreversible process (Gu et al., 2013).

It should be noted that plant root secretions contain metal chelating compounds that play an important role in rhizosphere pH regulation and metal-chelate reaction (Huang et al., 2020; Dong et al., 2007). Zhou et al., (2019) and Sasaki et al., (2014) confirmed that Cd could be fixed in root cell vacuoles and reduce Cd transport in rice. These studies, in agreement with the results of this research, confirm that it can reduce the absorption of Cd by the rice plant through the roots, which is also consistent with the achievements of Li et al., (2018) and Guo et al., (2018). In agreement with the findings of this study, Zhao et al., (2020) reported that the use of fly ash and its derivatives inhibited the absorption of Cd by the plant and, as a result, reduced its amount in the root, stem, leaf, rice husk and rice seed by 33.7, 41.2, 18.9, 27.6 and 20.8%, respectively. This may be because silica-based materials reduce the ultrastructural damage caused by pollution and poisoning and induce the formation of stronger organelles in the plant because the HM ions, after entering the cytoderm space of the cell by forming bonds with hydroxyl and carboxyl groups, lead to their deactivation. Another possible reason for this could be the combination of silica with Cd cation exchange sites, which leads to the formation of HM ions and cannot penetrate the protoplasm space, which leads to a decrease in the accumulation of these substances in rice seeds (Chen et al., 2019). Querol et al., (2006), Damian et al., (2013), and Feng et al., (2017) also demonstrated that the composition of intermediate materials and zeolite from ash should change the activity of soil enzymes and reduce the toxic effect of

Cd on rice by the silica present in their structure. They also stated that these materials, by deactivating the absorber of HMs in the roots, lead to a decrease in HMs absorption and reduce their amount in plant tissues. The results of this research indicated a significant effect of fly ash on soil pH in field experiments and pot experiments. Soil acidity directly affects the mobility of HM ions. After adding inactivators (passivators), the competition in the absorption of HM ions in the passivators decreases, and the negative charge of the soil increases, increasing soil pH, which was in agreement with the findings of Chen et al. (2019) and Li et al., (2018). Zhao et al., (2020) also reported that after adding fly ash, intermediate materials, and zeolite to the soil, its pH increased significantly compared to the control treatment. Some other studies (Li et al., 2018 and Balakhnina et al., 2015) also reported similar results and confirmed the positive and significant effect of fly ash and its derivatives on soil pH due to being rich in silica, which leads to a decrease in Cd which was absorbed by the rice. In general, when soil acidity changes from acidic to neutral, not only HM ions are absorbed by soil particles, but also hydrogen hydroxide deposits and chelate compounds are formed, which leads to their precipitation and reduces their absorption by plants (González-Núñez et al., (2012). After hydrolyzing silica in the soil, fly ash and its derivatives produce hydroxyl groups and are released into the soil, which is the main cause of increasing soil pH (Chen et al., 2019). Naderi et al., (2002) reported that the addition of fly ash leads to the stabilization of Cd in the soil, improves the soil's acidity, and leads to a decrease in the absorption of Cd by plants. Similar to the findings of this research, some researchers found that the cation exchange capacity plays an important role in controlling the dynamics of HM ions in the soil. In paddy fields where the soil has a low cation exchange capacity, Cd absorption is higher, which can be improved by using fly ash and its derivatives and preventing the absorption of Cd (Frohne et al., 2011; Zhao et al., 2020). Shaheen & Rinklebe (2015) reported that the cation exchange capacity in flooded soils such as rice paddies affected the mobility of HMs.

The results presented herein found that adding fly ash and its derivations was beneficial for yield performance and soil remediation. As well, some rice genotypes were appropriate for contaminated soils. Among these, intermediate materials strongly influenced soil properties, available Cd, rice organs, acid exchangeable fraction Cd, and growth performance. We have demonstrated that fly ash materials positively affect soil remediation and rice yield. However, in subsequent studies, it will need to explore further the factors involved above.

5. CONCLUSION

The general characteristic of fly ash, zeolite, and other derivatives is absorbing and retaining moisture in its texture. This causes the plant to have sufficient moisture available throughout its growth period and is less exposed to drought stress. Adding fly ash and its derivatives (intermediate materials and zeolite) increases soil silica and improves soil pH. It ultimately creates a complex with Cd in Cd-contaminated soils and prevents its absorption by plants. The present research results, the treatment of fly ash and its derivatives had a significant effect on rice yield.

Regarding the effect of genotype on rice yield, a significant effect was observed. Also, the interaction effect of fly ash and genotype treatment significantly affected rice yield. Based on the importance of rice production, the low price, and the availability of fly ash, these materials can increase rice yield, especially in soils contaminated with Cd. In addition to increasing the amount of the product, the toxic effects and Unfavorable Cd inhibited plant growth. As well the almost long-term effect of intermediates and their direct effect on increasing rice yield and yield components, the optimal method is economical and has high productivity. These results can be significant for possible remediation and eco-restoration of contaminated sites and plant performance.

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