

Original Research Article

Assessing the impact of altered clay mineral and red mud derivatives on the characteristics of Mustard (*B. juncea*) and the soil Arsenic content

ABSTRACT

A pot experiment was conducted during the winter season (rabi) of 2020-21 at ICAR-Indian Agricultural Research Institute, New Delhi. Indian mustard (*Brassica juncea*) was cultivated to investigate the impact of modified clay mineral (Bentonite) and Red mud on yield characteristics and total arsenic content in the soil. The main objective was to examine how the application of modified clay mineral and red mud (Fe-exchanged bentonite, Dimethyl sulfoxide-intercalated bentonite, and Iron-exchanged red mud) would affect the yield attributes of Indian mustard. The initial soil's total arsenic content was 16.2 mg kg⁻¹. The results revealed that all the mentioned treatments led to a significant increase in leaf biomass and root volume compared to the control pot. Significantly, highest leaf biomass (g pot⁻¹) was recorded in Fe-exchanged bentonite (4.10 g pot⁻¹) followed by Dimethyl sulfoxide-intercalated bentonite (4.00 g pot⁻¹), and Iron-exchanged red mud (3.93 g pot⁻¹) respectively at the rate of 5.00 g product per kg soil. The highest root volume (6.6 cm²) was observed in soil treated with 5.00 g kg⁻¹ of Fe-exchanged bentonite. Dimethyl sulfoxide-intercalated bentonite, and Iron-exchanged red mud also showed positive effects but to a lesser extent. total As content in contaminated soil was thoroughly investigated, and the results revealed that these clays did not exert a significant influence on the total As content under the given application rates.

Keywords: Brassica juncea, Clay minerals, Red mud, Arsenic

1. INTRODUCTION

Arsenic (As) is a naturally occurring element and is widely recognized as a toxic substance. Prolonged exposure to high levels of arsenic can lead to serious health issues, including various types of cancer, skin lesions, cardiovascular diseases, and other health problems. Arsenic is classified as a class-I carcinogen by the International Agency for Research on Cancer (IARC), meaning there is sufficient evidence of its carcinogenicity in humans. Contaminated drinking water is a significant source of exposure to arsenic in many regions worldwide. In more than 20 countries, including parts of South and Southeast Asia, South America, and certain areas in the United States, arsenic contamination in groundwater has been a major concern. This contamination can result from natural sources, industrial activities, or agricultural practices [1].

Arsenic and other heavy metal poisoning through crops and leafy vegetables is indeed a significant concern for human health and the environment. Heavy metals, including arsenic, can accumulate in plants from contaminated soil or water, and when consumed by humans, they can pose serious health risks. Various impacts of arsenic contamination on plants have been well-documented, including the suppression of growth, reduction in water potential,

hindered nutrient supply, impaired chlorophyll biosynthesis, decreased protein content, and a decline in photosynthetic efficiency, ultimately leading to reduced biomass accumulation. Mustard roots are susceptible to arsenic as it enters them by resembling phosphate, and rapidly transforms into As (III). Only a small proportion of arsenic makes its way to the above-ground tissues in mustard [2, 3].

To address heavy metal contamination, both biotic and abiotic methods can be employed. Biotic methods: These involve using living organisms such as plants or microorganisms to remediate or remove heavy metals from the environment. This process is known as phytoremediation when plants are used and bioremediation when microorganisms are employed. These organisms have the ability to take up or accumulate heavy metals, effectively reducing their concentration in the soil. Abiotic physicochemical methods: These are non-living processes that aim to remove or reduce heavy metals from contaminated soil. Some of the common abiotic methods include, Precipitation, Co-precipitation, Solvent extraction, Ion exchange, Reverse osmosis, Adsorption [4, 5, 6, 7]. Each of these approaches possesses distinct merits and constraints, and the selection of a remediation method relies on several factors, including the type of pollutant, the extent of contamination, site conditions, and cost-effectiveness. It is vital to employ suitable strategies to address heavy metal contamination and protect both human health and the environment.

Adsorption involves using a suitable adsorbent material (e.g., activated carbon, zeolites, clay mineral, redmud etc.) to attract and retain heavy metal ions on its surface, effectively removing them from the environment. Among the methods mentioned earlier, adsorption by clay minerals has proven to be exceptionally effective in eliminating arsenic contaminants from soil and water. It has garnered significant success due to its remarkable efficiency, affordability, adaptability, and speed. It is capable of operating effectively even at very low concentrations, making it suitable for both continuous and batch processes. Additionally, it produces minimal sludge, allows for recycling and reuse, and boasts low capital costs [5, 6, 7, 8]. The utilization of red mud as a means of environmental restoration presents several advantages, including cost-effectiveness, a straightforward process, and sustainable waste management. Both untreated and modified red mud have demonstrated effective adsorption capabilities for heavy metal ions in both soil and wastewater systems [7, 9, 10]. Consequently, employing modified clay mineral and red mud for immobilizing arsenic in soil holds promising prospects for further research.

2. MATERIAL AND METHODS

Soil sample was taken from the arsenic-affected region of Mitrapur (Nadia district) of West Bengal (22.9981 N, 88.6121 E). It receives 1385.3 mm of precipitation per year. Soil was collected from 0–15 cm depth and soil order was Inceptisols. The standard methods of preparing a soil sample and determining its physico-chemical parameters were followed (Table 1). Soil was digested with aqua-regia for determination of total As concentration in soil [11]. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (PerkinElmer NexION 300) was used to determine the As concentration in the digest. ICP multi-element standard solution which was supplied by Merck KGaA, Germany was used to calibrate the instrument. A reagent blank was prepared using a similar technique but without the sample. Using a combination electrode (glass and calomel electrodes) and a digital pH meter, the pH of soil was measured in a 1:2 (soil: water) solution [12]. Wet oxidation with $K_2Cr_2O_7$ was used to measure the amount of organic carbon of the soil [13]. The Bouyoucos approach was used to determine soil texture [14]. The ammonium acetate technique used to calculate the soil's cation exchange capacity (CEC) [15].

Table 1. Initial soil properties of the collected bulk soil sample

Soil characteristics	Contaminated soil
pH (1:2.5)	6.80
EC (dS m ⁻¹)	0.30
Soil texture	Sandy clay
% Sand	47.5
% Silt	9.2
% Clay	43.3
Soil organic carbon (g kg ⁻¹)	15.6
Cation exchange capacity (cmol (p ⁺) kg ⁻¹ soil)	27.5
Total As (mg kg ⁻¹)	16.2

2.1 Pot experiment

A pot culture experiment was carried out in the rabi season in 2020–21 at IARI, New Delhi using mustard (*B. juncea*) (Variety-Rohinga bullet) to evaluate the impact of modified clay mineral and redmud (Fe exchanged bentonite, dimethyl sulfoxide-intercalated bentonite, and Iron exchanged redmud) on mustard yield attributes and total arsenic concentration in the soil (Figure 1, 2). Three replications and a factorial complete randomised design were used to set up the pot experiment. In plastic pots with 4 kg of soil inside, various products were introduced at the rates of 0 (control), 1.25, 2.50, and 5.00 g kg⁻¹ soil. To sustain the plant population, total five plants were placed in each pot. Soil was watered with tap water to keep the field's capacity moisture level constant. The mustard crop provided a consistent application of the 80-40-40 kg ha⁻¹ N, P, and K fertiliser dosages that are advised normally in the local area. Following other advised agronomical practises, 50% of the nitrogen was administered as a basal dosage and the remaining doses were applied 30 days after planting.



Figure 1. Pot experiment (A. control pot; B, C and D are the treated pots by dimethyl sulfoxide-intercalated bentonite, Fe-exchanged bentonite and Fe-exchanged red mud respectively at the rate of 5.00 g kg^{-1})

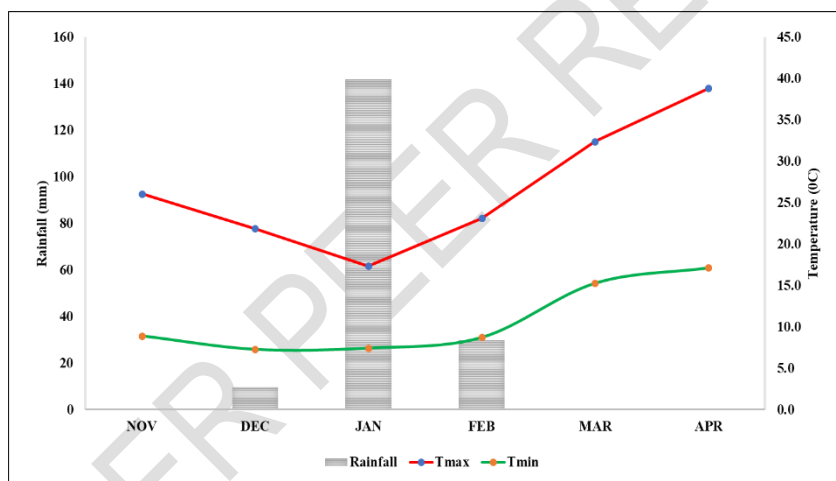


Figure 2. Monthly mean temperature and total rainfall variations during the mustard growing period at ICAR-IARI, New Delhi

3. RESULTS AND DISCUSSION

Soil treated with Fe-exchanged bentonite, DMSO-intercalated bentonite, and Iron-exchanged redmud resulted in significantly higher leaf biomass, and root volume (cm^2) of mustard plant (Tables 2, 3) as compared to the control pot. Significantly highest leaf biomass (g pot^{-1}) was recorded in Fe-exchanged bentonite (4.10 g pot^{-1}) followed by dimethyl sulfoxide-intercalated bentonite (4.00 g pot^{-1}), and Iron-exchanged redmud (3.93 g pot^{-1}) respectively at the rate of $5.00 \text{ g product per kg soil}$. Highest leaf biomass was recorded in Iron-exchanged redmud (3.63 g pot^{-1}) followed by Fe-exchanged bentonite (3.46 g pot^{-1}) and dimethyl sulfoxide-intercalated bentonite (3.32 g pot^{-1}), respectively at the rate of $2.50 \text{ g product per kg soil}$. Root volume was recorded highest in case of Fe-exchanged

bentonite (6.3 cm²) followed by Iron-exchanged redmud (5.9 cm²), and dimethyl sulfoxide-intercalated bentonite (5.4 cm²) respectively at the rate of 2.50 g product per kg soil. At the rate of 5.00 g product per kg soil root volume was followed the similar pattern as 2.50 g product per kg soil. Total arsenic concentration (mg kg⁻¹) in the soil after final harvesting of mustard was highest in case of iron exchanged bentonite (14.7 mg kg⁻¹) at the rate of 2.50 g product per kg soil followed by dimethyl sulfoxide-intercalated bentonite (14.6 mg kg⁻¹) and Iron-exchanged redmud (14.3 mg kg⁻¹) respectively. In this study, the impact of modified clay minerals and modified redmud, applied at varying rates of 0, 1.25, 2.5, and 5 g kg⁻¹ of soil, on the total As content in contaminated soil was thoroughly investigated, and the results revealed that these clays did not exert a significant influence on the total As content under the given application rates (Table 4).

This means that modified types of bentonites and redmud boost mustard productivity. So, we can say that, leaf biomass and root volume (cm²) of mustard plant was recorded at higher dose (2.5 and 5.0 g kg⁻¹ soil) of Fe-exchanged bentonite, dimethyl sulfoxide-intercalated bentonite, and Iron-exchanged redmud. Fe-exchanged bentonite, dimethyl sulfoxide-intercalated bentonite, and Iron-exchanged redmud did a good job of improving mustard biomass. The biomass (dry weight) of shoots generally reflects the tolerance ability of plants to unfriendly environments [16, 17]. Using less than 10 g kg⁻¹ sepiolite increased spinach productivity by 58.5 to 65.5 percent [17]. When the soil was spiked at 20 mg kg⁻¹, organoclays, i.e. bentonite treated with surfactants such HDTMA and Arquad-2HT75 @ 20%, decreased the bio accessible and bioavailable arsenic by 58 percent and 81 percent, respectively into the soil [5]. If we used 2% Na-bentonite and Ca-bentonite, which reduced heavy metal concentrations in wheat by 46 and 42 percent for Zn, 61 and 52 percent for Cu, and 56 and 65 percent for Ni, respectively, at 3rd harvest which increase the yield of plants [16]. Ferrihydrite decreased arsenic content in *B. campestris* from 1.84 to 0.97 mg kg⁻¹ according to [18]. Polymeric Al/Fe-modified montmorillonite lowers the pH, making it more favourable to arsenate adsorption [19, 20] as a result, the amount of arsenic in the soil was lowered. Although research on the use of modified clays in the soil and arsenic bioavailability in primary food crops and vegetables is limited, they do have an indirect effect on arsenic availability. The addition of clay minerals and redmud boosted microbial activity, whereas organic matter mineralization limited the availability of metals and metalloids to microorganisms [21]. Improved soil fertility could potentially be one of the causes for increased plant biomass in bentonite and redmud amended treatments.

Table 2. Effect of modified clay mineral and red mud on leaf biomass (g pot⁻¹) of mustard plant

Dose (g kg ⁻¹)	Fe-exchanged bentonite	Dimethyl sulfoxide-intercalated bentonite	Iron-exchanged redmud	Mean B
0	2.73	3.30	3.43	3.15
1.25	3.75	3.39	3.46	3.53
2.50	3.46	3.32	3.63	3.47
5.00	4.10	4.00	3.93	4.01
Mean A	3.51	3.50	3.61	

SE(m)	D- 0.20	C- 0.17	DxC- 0.35
LSD (≤ 0.05)	D- 0.59	C- N/A	DxC- N/A

C= Products; D= Dose of products

Table 3. Effect of modified clay mineral and red mud on root volume (cm^2)

Dose (g kg^{-1})	Fe-exchanged bentonite	Dimethyl sulfoxide-intercalated bentonite	Iron-exchanged redmud	Mean B
0	4.6	4.8	4.6	4.7
1.25	6.1	5.1	4.7	5.3
2.50	6.3	5.4	5.9	5.9
5.00	6.6	6.4	6.5	6.5
Mean A	5.9	5.4	5.5	
SE(m)	D- 0.31	C- 0.27	DxC- 0.54	
LSD (≤ 0.05)	D- 0.91	C- N/A	DxC- N/A	

C= Products; D= Dose of products

Table 4. Effect of modified clay mineral and red mud and their doses on total As concentration (mg kg^{-1}) in the soil after final harvesting of mustard

Dose (g kg^{-1})	Fe-exchanged bentonite	Dimethyl sulfoxide-intercalated bentonite	Iron-exchanged redmud	Mean B
0	14.3	13.9	14.1	14.1
1.25	13.8	13.8	13.8	13.8
2.50	14.1	13.9	13.9	14.0
5.00	14.7	14.6	14.3	14.6
Mean A	14.2	14.1	14.0	
SE(m)	D- 0.12	C- 0.14	DxC- 0.24	
LSD (≤ 0.05)	D- N/A	C- 0.40	DxC- N/A	

C= Products; D= Dose of products

4. CONCLUSION

The study demonstrates that the application of modified clay mineral and red mud (Fe-exchanged bentonite, Dimethyl sulfoxide-intercalated bentonite, and Iron-exchanged redmud) positively influenced the growth and yield characteristics of Indian mustard (*Brassica juncea*). These amendments, particularly Fe-exchanged bentonite, showed promising results in enhancing leaf biomass and root volume. However, regarding the total

arsenic content in the soil, the clays did not have a significant effect at the given application rates. These findings contribute valuable insights into potential soil amendments to improve crop productivity, but further research may be needed to explore their efficacy in arsenic-contaminated soil remediation.

REFERENCES

- [1] Sanyal SK, Gupta SK, Kukal SS, Jeevan Rao K. Soil degradation, pollution and amelioration. *State of Indian Agriculture-Soil*. National Academy of Agricultural Sciences, New Delhi. 2015;234-66.
- [2] Gusman GS, Oliveira JA, Farnese FS, Cambraia J. Arsenate and arsenite: the toxic effects on photosynthesis and growth of lettuce plants. *Acta Physiologiae Plantarum*. 2013;35:1201-9.
- [3] Shrivastava A, Ghosh D, Dash A, Bose S. Arsenic contamination in soil and sediment in India: sources, effects, and remediation. *Current Pollution Reports*. 2015;1:35-46.
- [4] Stojanovic A, Keppler BK. Ionic liquids as extracting agents for heavy metals. *Separation Science and Technology*. 2012;47(2):189-203.
- [5] Sarkar B, Naidu R, Rahman MM, Megharaj M, Xi Y. Organoclays reduce arsenic bioavailability and bioaccessibility in contaminated soils. *Journal of Soils and Sediments*. 2012;12:704-12.
- [6] Mukhopadhyay R, Manjaiah KM, Datta SC, Sarkar B. Comparison of properties and aquatic arsenic removal potentials of organically modified smectite adsorbents. *Journal of hazardous materials*. 2019;377:124-31.
- [7] Meena S, Chobhe KA, Manjaiah KM, Datta SP, Golui D, Meena AR and Saini R. Preparation and characterization of iron-exchanged red mud for arsenic adsorption efficiency. *The Pharma Innovation Journal*. 2022;11(2):1768-1771.
- [8] Meena S, Chobhe KA, Datta S, Manjaiah KM, Sharma VK. Effect of modified clay minerals and redmud on the bioavailability of arsenic. *Annals of Plant and Soil Research*. 2023;25(2):280-4.
- [9] Mench M. Physico-chemical aspects and efficiency of trace element immobilization by soil amendments. *Metal-contaminated soils: in situ inactivation and phytoremediation*. 1998:151-82.
- [10] Ma YF, Feng XD. The application of red mud on restoring heavy metal contaminated water and soil. *Advanced Materials Research*. 2011;225:1262-5.
- [11] Quevauviller P. Operationally defined extraction procedures for soil and sediment analysis I. Standardization. *TrAC Trends in Analytical Chemistry*. 1998;17(5):289-98.

- [12] Datta SP, Rao AS, Ganeshamurthy AN. Effect of electrolytes coupled with variable stirring on soil pH. *Journal of the Indian Society of Soil Science*. 1997;45(1):185-7.
- [13] Walkley A, Black IA. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil science*. 1934;37(1):29-38.
- [14] Bouyoucos GJ. Hydrometer method improved for making particle size analyses of soils 1. *Agronomy journal*. 1962;54(5):464-5.
- [15] Jackson ML. *Soil chemical analysis*, pentice hall of India Pvt. Ltd., New Delhi, India. 1973;498:151-4.
- [16] Usman AR, Kuzyakov Y, Lorenz K, Stahr K. Remediation of a soil contaminated with heavy metals by immobilizing compounds. *Journal of Plant Nutrition and Soil Science*. 2006;169(2):205-12.
- [17] Sun Y, Sun G, Xu Y, Wang L, Liang X, Lin D. Assessment of sepiolite for immobilization of cadmium-contaminated soils. *Geoderma*. 2013;193:149-55.
- [18] Sun Y, Liu R, Zeng X, Lin Q, Bai L, Li L, Su S and Wang Y. Reduction of arsenic bioavailability by amending seven inorganic materials in arsenic contaminated soil. *Journal of Integrative Agriculture*. 2015;14:1414-1422.
- [19] Ramesh, A., Hasegawa, H., Maki, T. and Ueda K. Adsorption of inorganic and organic arsenic from aqueous solutions by polymeric Al/Fe modified montmorillonite. *Separation and Purification Technology*. 2007;56:90-100.
- [20] Su J, Huang HG, Jin XY, Lu XQ, Chen ZL. Synthesis, characterization and kinetic of a surfactant-modified bentonite used to remove As (III) and As (V) from aqueous solution. *Journal of hazardous materials*. 2011;185(1):63-70.
- [21] Usman, A.R.A., Kuzyakov, A.Y. and Stahr, Y.K. Effect of clay minerals on extractability of heavy metals and sewage sludge soil mineralization in soil. *Chemistry and Ecology*. 2004;20:123-135.