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Immobilization of arsenic in soil using modified bentonite and red mud to reduce its bio-availability in *Brassica juncea*

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Arsenic (As) is widely distributed in soil, originating either from natural sources like As containing parent material or from anthropogenic sources. Both organic and inorganic As species have been identified in terrestrial plants, with arsenate [As(V)] and arsenite [As(III)] being the most dominant (Francesconi *et al.* 2002). Arsenic poisoning to humans from crops and leafy vegetables (i.e. mustard, lettuce) is a current topic of concern. As pollution in plants is found to inhibit growth, water potential, nutrient availability, chlorophyll production, protein content, and a decrease in photosynthetic efficiency, and biomass formation (Gusman *et al.* 2013, Shrivastava *et al.* 2015).

To reduce the harmful effects of heavy metals on the environment, we need to reduce the solubility and bioavailability of heavy metals without removing them from soil (Ma and Rao 1997). Phosphate minerals, Fe and Mn oxides, red mud, aluminosilicates, and coal fly ash are some examples of natural and artificial additives that can be used to immobilize arsenic (Mench *et al.* 1998, Ma and Feng 2011, Meena *et al.* 2022). Some physicochemical processes such as precipitation, co-precipitation, solvent extraction, ion exchange, reverse osmosis and adsorption of the heavy metal also help in immobilizing arsenic (Celis *et al.* 2000). Among them adsorption has been found to be one of the efficient methods for reducing plant uptake of As from soil because of its highly effective and rapid nature, affordability, adaptability, applicability at very low concentrations, little sludge generation, recycling and reuse possibilities, and low capital costs (Sarkar *et al.* 2012, Mukhopadhyay *et al.* 2017). Some studies claimed that modified clay minerals and red mud can reduce the plant uptake of As from soil (Sarkar *et al.* 2012, Raj *et al.* 2017, Yang *et al.* 2022). Red mud exhibits the qualities of being inexpensive, easy to use, and waste-controlling by-waste when used as environmental restoration material. Modified red mud is effective at removing heavy metal ions from contaminated soil and water systems (Ma and Feng 2011). Hence, the use of modified clay minerals and red mud for immobilizing As in soil offers a potential research area.

A pot experiment was conducted at ICAR-Indian Agricultural Research Institute, New Delhi, during winter (*rabi*) season (2020–21) using *Brassica juncea* L. (V. Rohinga bullet) as a test crop to evaluate the effect of modified clay mineral and red mud product (Fe exchanged bentonite, DMSO intercalated bentonite and Iron exchanged red mud) on plant uptake of arsenic. The bulk soil for the experiment was collected from the arsenic contaminated area of Mitrapur, Nadia, West Bengal (22.9981°N, 88.6121°E). Soil physico-chemical properties were measured by the standard methods. Soil was extracted with 0.5 M $NaHCO_3$, *p*H 8.5 (Olsen *et al.* 1954) for extractable As content. Using a digital *p*H meter and combined electrodes, the *p*H of soil in a 1:2 (soil:water) suspension was determined (Datta *et al.* 1997). The amount of organic carbon in soil was measured using the wet oxidation method described by Walkley and Black (1934). The Bouyoucos (1962) method was used to determine soil texture. Ammonium acetate method was used to calculate the cation exchange capacity (Jackson 1973). Arsenic concentration in mustard samples was determined by using a microwave digester with concentrated (65%) suprapure nitric acid (Guven and Akinci 2010). ICP-MS (Inductively Coupled Plasma Mass Spectrometry) was used to determine the total amount of As in the digest. Initial soil organic carbon content, *p*H and EC were 15.6 g/kg, 6.8 and 0.30 dS/m respectively. Soil was sandy clay in texture with cation exchange capacity 27.5 cmol (p^+) per kg. Olsen extractable As and total As were found to be 3.1 mg/kg and 16.2 mg/kg respectively. Experiment was laid out in a factorial completely randomized design with three replications. Different products at the rate of 0, 1.25, 2.50, and 5.00 g/kg doses were added in pots containing 4 kg soil. Five plants per each pot were used to maintain a uniform mustard population.

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Hazard quotient (HQ): The HQ was determined to evaluate the potential noncarcinogenic risk associated with the consumption of As from contaminated mustard.

$$HQ=ADD/RfD$$

The hazard quotient is a numerical representation of the risk associated with exposure to As, calculated as the ratio between the average daily dose (ADD; mg/kg/d) of As and its reference dose (RfD; mg/kg/d). The reference dose is the highest daily intake of As that can be tolerated without causing any adverse health effects (Roy *et al.* 2023).

Preparation of modified clay minerals and red mud: The unmodified smectite and red mud samples were purchased from S D Fine-Chem Limited, Mumbai, India. The clay samples contain 88% smectite as the main mineral composition (kaolinite and quartz as impurities). For modification of bentonite, we used 0.1 M $FeSO_4 \cdot 7H_2O$ solution method as described by Mukhopadhyay *et al.* (2017). The bentonite–DMSO intercalation complex was made following the method given by Zhang *et al.* (2012). The raw red mud was modified using $FeCl_3$ solution as described by Meena *et al.* (2022).

Plant growth parameter: Soil treated with Fe exchanged bentonite, DMSO intercalated bentonite and Fe exchanged red mud resulted in significantly higher biological yield (g/pot) as compared to control pot (Table 1). Between the treatments, significantly higher biological yield (g/pot) of mustard plant was recorded at higher dose (2.5 and 5.0 g/kg soil). The shoot arsenic concentration was reduced below the phytotoxicity range. Accordingly, the shoot dry-matter production was increased. A study conducted by Sun *et al.* (2013) also showed that incorporating less than 10 g/kg of sepiolite resulted in a noteworthy boost in spinach productivity, ranging from 58.5–65.5%. Additionally, the growth of shoots in plants is often indicative of their capacity to withstand adverse conditions, as stated by Usman *et al.* (2006).

Arsenic concentration in soil: The amendments such as, Fe-bentonite, DMSO-bentonite and Fe-red mud showed significant positive effect on extractable As reduction in the soil (Table 2). At 1.25 g/kg dose of application, Fe-red mud was found effective for abatement of As contamination in soil (soil As concentration 2.71 mg/kg) with no significant difference with other two modified clay minerals. In the study, it was found that when Fe-red mud was applied to the soil at both 2.50 g/kg and 5.00 g/kg rates, it retained the highest concentration of extractable arsenic compared to other products. On the other hand, DMSO-bentonite and Fe-bentonite were shown to be the most effective in reducing the extractable arsenic concentration in the soil when applied at the rates of 2.50 g/kg and 5.00 g/kg, respectively. Similarly, Sarkar *et al.* (2012) reported that when the soil was spiked at 20 mg/kg, organoclays, i.e. bentonite treated with surfactants such HDTMA and Arquad 2HT-75 at the rate of 20%, decreased the bio accessible and bioavailable arsenic by 58 and 81%, respectively. Sun *et al.* (2015) also found that ferrihydrite-treated soils exhibited a 67 and 20% reduction in non-specifically adsorbed As and available-As, respectively, when compared to control soils.

Bioavailability of arsenic from soil: Effect of soil application of modified clay minerals and red mud on As concentration (mg/kg) in mustard leaves at harvesting stage is presented in Table 3. The data clearly depicted that all the products, by increasing their doses of application, significantly reduced the arsenic concentration in mustard leaves. Among all the products, DMSO-bentonite when applied in soil both at the rate of 1.25 and 2.50 g/kg retained highest arsenic concentration as compared to other products, whereas Fe-bentonite and Fe-red mud were proved to be most effective in reducing the arsenic concentration in mustard leaf at the rate of 1.25 g/kg and 2.50 g/kg doses of application respectively. Fe-bentonite, when applied at the rate of 5.00 g/kg, retained the lowest concentration of arsenic (i.e. 0.59 mg/kg) in mustard leaves at the harvesting stage. Arsenic in soil is retained by its parent materials, chemical bonding with clay and organic matter, or potentially through biological interactions. The introduction of modified clay and red mud enhances the chemical binding of arsenic, leading to reduced mobility and slower release in the soil due to its strong adsorption with clay particles and red mud. Usman *et al.* (2006) also used 2% Na-bentonite and Ca-bentonite, which reduced heavy metal concentrations in

Table 1 Effect of modified clay mineral and red mud on biological yield (g/pot) of mustard

Dose (g/kg)	Fe-bentonite	DMSO-bentonite	Fe-red mud	Mean B
0 (control)	7.8	8.4	8.5	8.3
1.25	9.0	9.0	9.2	9.0
2.50	9.5	8.8	9.5	9.3
5.00	11.2	10.9	11.1	11.1
Mean A	9.4	9.3	9.5	
SEm±	D- 0.38 C- 0.33 D×C- 0.66			
LSD (P≤0.05)	D- 1.12 C- N/A D×C- N/A			

C, Products; D, Dose of products.

Table 2 Effect of modified clay mineral and red mud and their doses on extractable As concentration (mg/kg) in soil after final harvesting of mustard

Dose (g/kg)	Fe-bentonite	DMSO-bentonite	Fe-red mud	Mean B
0 (control)	3.03	3.05	2.95	3.01
1.25	2.79	2.83	2.71	2.78
2.50	1.87	1.82	1.88	1.85
5.00	0.90	1.23	1.28	1.14
Mean A	2.15	2.23	2.21	
SEm±	D- 0.06 C- 0.05 D×C- 0.11			
LSD (P≤0.05)	D- 0.18 C- N/A D×C- N/A			

C, Products; D, Dose of products.

Table 3 Effect of modified clay mineral and red mud and their doses on As concentration (mg/kg) in plant leaf at harvesting stage

Dose (g/kg)	Fe-bentonite	DMSO-bentonite	Fe-red mud	Mean B
0 (control)	1.81	1.74	1.77	1.77
1.25	1.54	1.66	1.62	1.61
2.50	0.95	0.99	0.93	0.96
5.00	0.59	0.71	0.72	0.68
Mean A	1.23	1.28	1.26	
SEm±	D- 0.02 C- 0.02 C×D- 0.03			
LSD (P≤0.05)	D- 0.05 C- N/A C×D- 0.09			

C, Products; D, Dose of products.

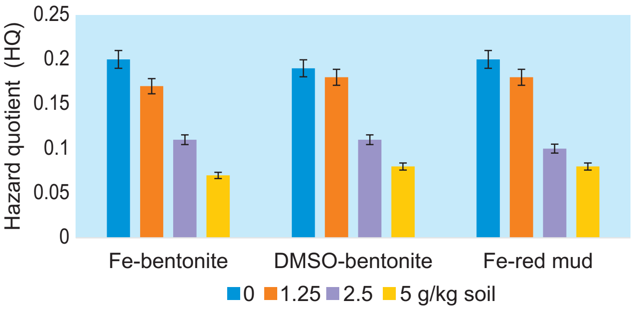

Fig 1 Hazard quotient values for arsenic in mustard under modified bentonite and red mud treatments added to the soils in pot at the rates of 0, 1.25, 2.5, 5.00 g/kg soil.

wheat by 46 and 42% for Zn, 61 and 52% for Cu, and 56 and 65% for Ni, respectively, at 3rd harvest. Ferrihydrite decreased arsenic content in *B. campestris* from 1.84–0.97 mg/kg (Sun *et al.* 2015).

Hazard quotient: Because leafy green vegetables are grown and sold in the research region, the HQ for human arsenic exposure from mustard leaf consumption was calculated (Fig 1). The HQ of mustard leaf in control treatments showed 0.20, 0.19 and 0.19 in Fe-bentonite, DMSO-bentonite and Fe-red mud respectively. The HQ of mustard leaf in lower and moderate treatment application showed 0.17, 0.18 and 0.18 in Fe-bentonite, DMSO-bentonite and Fe-red mud respectively, but after the application of treatments at higher dose (5 g/kg soil) the hazard quotient significantly reduced by 0.07, 0.08 and 0.08 respectively. Fe-bentonite, DMSO-bentonite and Fe-red mud applied at 2.50 or 5.00 g/kg decreased the As concentration in mustard leaf, resulting in lower HQ values for As consumption by humans through mustard leaf in the study area. All modified products decreased As content in leaf, leading to lower HQ values for human intake of arsenic through these leaves. Similar results were also reported by Mandal *et al.* (2012), they stated that mustard leaf had HQ values greater than 1 in naturally polluted soil due to arsenic availability, making them unsuitable for consumption, which can be significantly reduced by application of modified clay minerals in the leafy plants (Kumararaja *et al.* 2017).

SUMMARY

The influence of modified clay mineral and red mud on biological yield and arsenic bioavailability to mustard were investigated. The total biomass of the mustard was increased by application of clay mineral and red mud products. At higher doses (5.00 g/kg), Fe-bentonite treated soil recorded the highest total plant biomass (11.2 g/pot). DMSO-bentonite (1.23 mg/kg) and Fe-bentonite (1.28 mg/kg) were proved to be most effective in reducing the extractable arsenic concentration in soil at the rate of 5.00 g/kg doses. These products also help in lowering the hazard quotient (0.20–0.08) values for human consumption of arsenic through mustard leaf. This means that modified types of bentonites and red mud boost mustard productivity by reducing arsenic concentration.

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