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Preparation and characterization of iron-exchanged redmud for arsenic adsorption efficiency

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Abstract
This study investigated the effectiveness of raw redmud and iron exchanged redmud for arsenic (As) adsorption efficiency at different time intervals. Due to the raw red mud's low arsenic absorption efficiency percentage, alkaline nature, less specific surface area, and poor selectivity, unmodified redmud are less effective than modified redmud in capturing arsenic from contaminated environments. Iron exchanged redmud have been developed to absorb arsenic in contaminated environments. Scanning electron microscopy (SEM), Specific surface area (SSA), and Cation exchange capacity (CEC), were used to analyse the surface morphology, composition, surface area and surface charge of the raw and Iron-exchanged redmud. Adsorption efficiency of arsenic on raw redmud and iron exchanged redmud were studied in a controlled laboratory condition at various times. Iron exchanged redmud was shown to be more successful in arsenic adsorption efficiency than raw redmud in the study.

Keywords: Red mud, modified redmud, remediation, arsenic, adsorption efficiency

Introduction
Arsenic (As) is classified as a class-I carcinogen and its hazard in drinking water has been reported from more than 20 countries (Sanyal *et al*., 2015) [17]. Arsenic pollution is becoming a major problem in the world these days, owing to its widespread distribution in the environment. In this context, As-polluted groundwater of Bengal delta basin comprising Bangladesh and West Bengal (India), bound by the rivers Ganga and Padma, has a great significance (Sanyal *et al*., 2015) [17]. More than 70 countries are reported with natural As contamination posing a serious health hazard to an estimated 150 million people, around 110 million of which live in Bangladesh, China, Cambodia, India, Laos, Myanmar, Nepal, Taiwan, Pakistan and Vietnam (H. Brammer and P. Ravenscroft 2009) [3].

Excessive intake of as in drinking water and food for long periods of time causes food-chain contamination, which can lead to serious health problems including pigmentation and keratosis. Arsenicosis is associated with a variety of health issues, including weakness, liver fibrosis, peripheral vascular disease, conjunctivitis, cardiovascular diseases, chronic respiratory disease, peripheral neuropathy, gangrene, skin cancer, pre-malignant skin lesions, bladder and lung cancer (Golui *et al*., 2017a) [5]. Arsenic poisoning by crops and leafy vegetables is a major immediate concern for humans and other living things. Inhibition of growth, water potential, nutrient supply, chlorophyll biosynthesis, protein content and decrease in photosynthetic efficiency as well as biomass accumulation are all documented effects of arsenic contamination in plants (Gusman *et al*., 2013; Shrivastava *et al*., 2015) [6, 20]. Arsenic (As) contamination of soils and groundwater can result from a variety of natural (e.g., natural geochemical reactions) and anthropogenic (e.g., application of agricultural pesticides mining, discharges of industrial wastes and military activities) sources (Zhang *et al*., 2009) [25]. The availability of As in soil has been found to be affected by a number of parameters, including soil type, pH, redox potential, solid-solution equilibria, organic matter content, and the presence of other ions in soil solution (Mandal *et al*., 2019) [11].

Researchers are concentrating their efforts on removing arsenic using a variety of techniques such as precipitation, flocculation (Lakshmanan *et al*., 2008; Hesami *et al*., 2013; Rashidi Nodeh *et al*., 2016) [9, 7, 16], adsorption (Mukhopadhyay *et al*., 2019) [13], ion exchange, membrane filtration, bioremediation, and advanced treatment methods such as ozonation and electrochemical methods. However, there are just few technologies for removing arsenic from contaminated soils.

Precipitation procedures produce large quantities of heavy metal-laden sludge, while ion-exchange and electrochemical methods are inefficient for large volumes of water, and membrane filtration is expensive due to membrane fouling (Stojanovic and Keppler, 2012) [23]. Because of the membranes spoil quickly and must be replaced frequently, reverse osmosis is a costly technique. However, many of these methods are costly and still do not have standard procedure of practical soil application.

Adsorption has been one of the best methods for removing arsenic from soil and water, because it has been found to be extremely efficient, affordable, versatile, and rapid, little sludge generation, recycling, and recycle potentials. Red mud is a type of solid wastes generated during the aluminium smelting process. Because red mud contains more chemical alkali, metal oxide, and radioactive substance, it is difficult to use it in a safe manner (Smiciklas *et al.*, 2014) [21]. Many scientists all over the world have been paying growing attention to the use of red mud in recent years, but they have been a little disappointed (Shirzad-Siboni *et al.*, 2014) [19]. Thus, it is necessary to search for a strategic approach for increasing use of red mud for as adsorption.

Materials and Methods
A. Preparation of iron-exchanged redmud
A $FeCl_3$ solution (which were purchased from Sigma-Aldrich Chemicals Pvt. Ltd., New Delhi, India) was used to modify the red mud. Redmud was quantitatively added to 200 ml of 1 M $FeCl_3$ solution under stirring circumstances until the slurry pH reached 8.0. The modified red mud was dried out in the open air before being crushed and sieved into particles with a diameter of less than 1 mm. Iron-exchanged redmud was the final product, which was labelled and stored in dry, clean containers for future use (Liang *et al.*, 2010) [10].

B. Characterization of redmud

Table 1: Different parameters for characterization of redmud

Parameters	Methods/Instruments	References
Specific Surface Area	EGME method	Carter *et al.* (1965) [4]
Surface charge	Cation exchange capacity (CEC)	Jackson (1973) [8]
Surface morphology	Scanning electron microscopy (SEM)	Smith and Oatley (1955) [22]

Specific surface area
A total of 200mg of clay was weighed into a tared aluminium can with a lid, and the sample was distributed uniformly over the bottom. The can was put in a vacuum desiccator with the lid beneath over about 250 g of P_2O_5. The desiccator was vacuumed for one hour and dried to constant weight. Clay-adsorbate slurry was formed by wetting samples with approximately 2 mL of reagent-grade ethylene glycol monoethyl ether (EGME) and placing them over the $CaCl_2$ - EGME solvate. A vacuum desiccator containing $CaCl_2$ was used to dry the entire culture chamber. After allowing 30 minutes or more for the sample solvate slurry to equilibrate, the desiccator was evacuated with a vacuum pump for about 45 minutes. Weighing the can, lid, and sample, the culture chamber was returned to the desiccator, and the desiccator was returned to the culture chamber. A vacuum pump was used to evacuate the desiccator for 45 minutes. The samples

were weighed at 2 to 4 hour intervals, with evacuating in between, until they reached a constant weight. Calculation of specific surface was done by the equation (Carter *et al.* 1965) [4]

$$A= Wa / (WS \times 0.000286)$$

where A- specific surface in m 2/g, Wa- weight of ethylene glycol monoethyl ether (EGME) retained by the sample in g, Ws-weight of P_2O_5-dried sample in g, and 0.000286 is the weight of EGME required to form a monomolecular layer on a square meter of surface.

Cation exchange capacity (CEC)
The CEC of clays was calculated using Jackson's method (1973). 200 mg of clay was placed in a centrifuge tube with 10 ml of 0.25M $CaCl_2$ solution and centrifuged at 5000 rpm for 10 minutes. The supernatant was decanted, and the procedure was performed four times further. The sample was then washed twice with distilled water (10 mL), twice with 50 percent acetone (10 mL), and twice with 80 percent acetone to remove chloride. The washing procedure was continued until the sample was free of chloride, which was confirmed by treating the supernatant liquid with $AgNO_3$. 10 mL of 0.25M $MgCl_2$ was added to the chloride-free sample and centrifuged for 10 minutes at 5000 rpm. In a 100 mL volumetric flask, the supernatant was collected. The supernatant was collected after two further repetitions of the previous step. Using distilled water, the volume was set at 100 mL, and the Ca concentration in the 100 mL supernatant was measured by AAS.

Scanning electron microscope (SEM)
The scanning electron microscope generates a variety of signals at the surface of solid specimens using a directed beam of high-energy electrons. External morphology (texture), chemical composition, and crystalline structure and orientation of materials that make up the sample are all revealed by the signals derived from electron sample interactions. In most cases, data is collected over a specific region of the sample's surface, and a 2-dimensional image is created to show spatial differences in these properties. Conventional SEM techniques can image areas ranging from 1 cm to 5 microns in width in a scanning mode (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). EVO / MA10 scanning electron microscopy was used to determine morphology and surface composition (CARL ZEISS Instrument). Prior to analysis, the powder samples were placed on dual-sided carbon tape covered copper stabs with industrial glue and coated with 20 nm thick palladium layers under a vacuum of 1.7 e $^{-0.005}$m bar (10^{-3} Torr).

Adsorption studies
Redmud (0.5 g) was weighed and taken in plastic centrifuge tubes (50 mL). Arsenic solutions (10 mL) of 50 µg mL^{-1} concentration in 0.01 M $CaCl_2$ was then added into the tubes. The suspensions were equilibrated for 24 h on an end over end shaker (225 rpm) to ensure the equilibrium. The experiment was conducted in triplicate at 20 °C and pH 6.0 (Maintained with 0.1 N HNO_3 and 0.1 N NaOH). After equilibration, the supernatants were separated and analysed for as concentrations by atomic adsorption spectra method (AAS). Blank tests under the same conditions revealed no As

adsorption on the tube wall during the reaction period. The As adsorption efficiency (%) was calculated using Eq. 1:

$$\text{Adsorption efficiency (\%)} = \frac{(C0 - Ce)}{C0} \qquad \text{Eq. 1}$$

Where, C_0 is the As concentration ($\mu g\ mL^{-1}$) at time zero; Ce is the equilibrium As concentration ($\mu g\ mL^{-1}$) at time t (Mukhopadhyay *et al*., 2017) [14].

Results and Discussion
A. Physiochemical properties
Table no. 2 shows some of the physicochemical properties of raw and iron-exchanged redmud. Most notably, pH of the raw redmud and iron-exchanged redmud plays a significant role in arsenic adsorption. The raw redmud (pH 12.5) was alkaline in nature. After reactions of redmud with $FeCl_3$, the pH values reduced to 8.0. The pH of iron-exchanged redmud was reduced because of saturation of the redmud with iron (Liang *et al*., 2010) [10]. The SSA of the redmud increased from 16.5 to 19.7 $m^2\ g^{-1}$ after modification with $FeCl_3$ solution. Specific surface area of kaolinite and smectite was increased by inorganic modified (Adebowale *et al*., 2006) [1]. The improvement in SSA in clay products was most likely caused by the removal of impurities from clay minerals (Rusmin *et al*., 2016). Additionally, the displacement of exchangeable cations, notably Fe^{2+}, may have exposed the clay edges and enhanced the SSA (Akpomie and Dawodu, 2016) [2]. The cation exchange capacity (CEC) of the redmud was 47.5 cmol (p+) kg^{-1}, whereas these values were 45.7 after inorganic modification. Because the guest cations, long chained surfactant, and iron may have blocked the adsorption sites, the CEC of modified smectite dropped following the exchange and pillaring operations (Mukhopadhyay *et al*., 2017) [14].

Table 2: Physiochemical properties of redmud

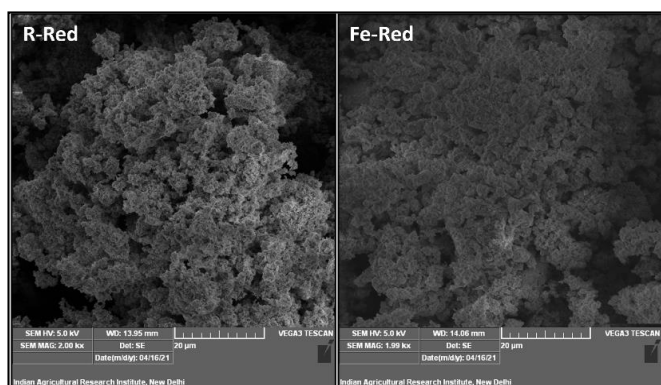| S. No.	Treatments	pH (1:2.5)	Specific surface area ($m^2\ g^{-1}$)	CEC (cmol (p+) kg^{-1})
1	Raw Redmud	12.5	16.5	47.5
2	Iron -exchanged redmud	8.0	19.7	45.7

B. Scanning electron microscope (SEM) characterization
SEM was used to examine the morphology of red mud and iron-exchanged red mud. The red mud was composed of course, angular, and irregular particles, as illustrated in Figure no. 1, and it had a large fracture and divaricate structure on its surface. The size of the fracture in iron-exchanged red mud was less than that of raw red mud, and many nearly spherical particles emerged on the surface of modified red mud. The iron-exchanged redmud showed porous and rough surfaces after modification. The intercalation of Fe and Cu complexes reduced the intensities and broadened the kaolinite characteristic peaks, particularly under hydrothermal conditions (Zhou *et al*., 2018) [26].

Fig 1: SEM images of raw redmud (R-Red) and iron-exchanged redmud (Fe-Red)

Adsorption efficiency (%) of arsenic for raw redmud and iron-exchanged redmud in aqueous systems
Irrespective of the redmud and iron-exchanged redmud types, the adsorption efficiency (%) was significantly increased with increasing time of adsorption (Table 3). Adsorption efficiency (%) was lowest in both products at the 15minuts**.** Among the unmodified and iron-exchanged redmud, iron-exchanged redmud showed maximum adsorption efficiency at time 120 mins (55.59%) followed by unmodified redmud (49.71%). During interaction with water in the interlayer and oxygen atoms at the end of each sheet of the clay mineral, the exchanged iron in the interlayer of bentonite more probably formed iron hydroxides and oxides through oxidation and hydration processes (Stucki *et al*., 2002) [24]. Previous studies using crystalline hydrous ferric oxide had found a faster adsorption mechanism (Manna *et al*., 2003) [12]. Multiple adsorption processes were present, including anion exchange, and high surfactant loading resulted in the formation of a positive surface charge that electrostatically binds arsenate (Sarkar *et al*., 2010b) [18].

Table 3: Adsorption efficiency (%) of arsenic for raw redmud and iron-exchanged redmud in aqueous systems

Times (Minutes)	Treatments		Mean
	Raw redmud	Iron-exchanged redmud	
15	44.40	50.47	47.43
30	46.42	52.65	49.54
60	48.82	54.22	51.52
90	49.62	55.58	52.60
120	49.72	55.59	52.65
Mean	47.79	53.70	
C.D.	R-1.06, T-1.68, R*T- N/A		
SE(d)	R-0.50, T-0.80, R*T- 1.13		
SE(m)	R-0.36, T-0.56, R*T- 0.78		
R- Redmud, T-Time			

Conclusions
Iron-exchanged redmud were successfully prepared and were reported to be an effective amendment for remediation of arsenic contaminated system. Raw redmud and Iron-exchanged redmud were found to be effective for arsenic immobilization. among them, Iron-exchanged redmud was found to be the most effective in arsenic adsorption efficiency (%). Scanning electron microscope, Specific surface area, CEC analysis have shown that there were detectable changes in the surface morphology, composition, surface area and surface charge of the Iron-exchanged redmud. The raw redmud was strong alkaline in nature but after reactions of redmud with $FeCl_3$, the pH values reduced. Though more research is needed to provide a full explanation of the

findings, liming qualities and a higher concentration of Fe and Al oxides in raw redmud and iron exchanged redmud could explain why it is a more effective arsenic immobilising agent.

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