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Efficient loading of nano Mn particles on calcined laterite soil (Lt-nMn) for higher removal of As(III) ions from groundwater: Adsorption and eco-scale analysis

By

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Abstract: Occurrence of arsenic in the groundwater has become a cause for concern in many countries. The presence of As(III) species in the groundwater had been one of the biggest challenges for the water workers especially in the south east Asian countries. Nano based adsorption techniques are gaining attention among researchers for the removal of arsenic ions. However, synthesis of nano-adsorbents is a costly affair. Therefore, the present study utilized the cheap and readily available laterite soil as a base material for nano coating. Nano sized manganese (nMn) particles were synthesized by chemical reduction method and later coated on calcined laterite (Lt-nMn). Coating with 0.1 M nMn provided the best As(III) removal efficiency. The prepared material was characterised for its morphological and surface properties. Phase analysis using XRD (X-ray diffraction) showed the presence of zero valent manganese species, which assisted in adsorption. Adsorption studies were conducted by selecting the different affecting parameters such as contact time, concentration, dose, temperature, and pH. Very high removal in less time regime led to the investigation of the oxidation mechanism. Phosphate and sulphate anions insignificantly reduced the removal efficiency. Langmuir model for the sorption isotherms and pseudo-second order kinetic model for the sorption kinetics symbolized the experimental data. Sustainability studies in terms of eco-scaling and cost analysis were performed for the applied method of production of the nano materials. Adsorber design analysis was also conducted to estimate the required amount of Lt-nMn particles for achieving the desired equilibrium As(III) concentration.

Keywords: Adsorption; As(III) removal; Batch adsorber design; nano Manganese particle; and Laterite.

1. Introduction

Arsenic is a potentially toxic element even at low concentrations, generally found in groundwater due to weathering of arsenic-bearing minerals, overuse of arsenic-contained pesticides, and industrial discharge (Smedley and Kinniburgh, 2002). People of a wide geographic region including several countries such as Bangladesh, India, Vietnam, China, Nepal, Pakistan, Chile, Cambodia, Hungary, Canada, Germany, United States of America, Argentina, and Mexico are suffering from this groundwater-poison (Nguyen et al., 2020 ; Mondal et al., 2008) . Arsenite [As(III)] and arsenate [As(V)] are the two major inorganic arsenic species generally found in natural groundwater of arsenic contaminated areas. The occurrence of these species depends on groundwater chemistry such as redox potential, pH, and concentration of other dissolved ions (Thanh et al., 2016). As(III) predominates in the groundwater where reducing and anaerobic conditions occur due to the presence of organic matter and high sulphate content. Whereas, the As(V) is expected to be present under alkaline environment in arid to semi-arid climates (Mukherjee et al., 2018). As(III) is more toxic and for being a neutral species, it is more difficult to remove by any treatment technology (Zhang et al., 2017). Intake of arsenic contaminated water can lead to cancers in different vital organs. Considering the potential carcinogenic effect, the permissible limit of arsenic in drinking water has been recently reduced to 10 ppb from 50 ppb in India (BIS, 2012). A treatment technology that can simultaneously remove both As(III) and As(V) with high removal efficiency is essentially desirable.

Several arsenic removal technologies such as ion exchange, membrane filtration, adsorption, coagulation and precipitation have been tried by researchers worldwide. Out of these technologies, adsorption is drawing more attention from the researchers owing to the involvement of low cost, high removal efficiency, safer to handle, low sludge production, simplicity in design, and easier applicability in the rural area (Lata et al., 2019).

In particular, iron-based adsorbents have been the most favoured candidate for arsenic removal. It was also witnessed that the As(V) is easy to remove from groundwater. Hence, it is most often advised to oxidise As(III) ions into As(V) before their adsorption. Application of nanomaterials as an adsorbent for arsenic removal is also very trendy and

popular among water scientists. Nevertheless, the synthesis of these nano materials has always been a matter of concern in terms of eco friendliness and cost. Additionally, the separation after treatment and low permeability in flow-through conditions are some of the inherent problems of nano adsorbent application. This can be avoided if nano adsorbents are incorporated into suitable and cost-effective host matrix such as soil, and sand.

Application of manganese and iron in combination can solve the problem associated with the As(III) removal. Manganese and iron oxide minerals are commonly found in soil and reported to have the high oxidizing potential of As(III) and adsorption of arsenic (Wang et al., 2015). The use of Fe-Mn binary oxides for adsorption of arsenic is gaining interest among the researchers as oxides of iron are well reported to have strong affinity and selectivity for arsenic (Wen et al., 2017; Ge et al., 2016). Particularly the nano sized manganese can facilitate the smoother oxidation and adsorption of As(III) ions. Integration of this nano-manganese with the iron particles is seemingly a viable option for arsenic treatment. However, the iron particles need not be present in the nano form. This may increase the cost of synthesis and application. Hence, the readily available and cost-effective source of iron must be selected. Among various iron minerals, laterite is abundantly available in nature and has been extensively studied as a potential adsorbent for arsenic removal (Partey et al., 2008). A combination of nano form of manganese and laterite soil as a host matrix can solve the problems of As(III) removal as well as the nano material application. Thus, for the present study, a noble adsorbent was prepared by coating laterite (Lt) with nano manganese particles (nMn) (Lt-nMn adsorbent) to remove higher amount of As(III) ions from groundwater. The removal behavior of As(III) by Lt-nMn adsorbent was assessed and optimized by observing the effect of each parameter affecting the adsorption process. Severity of the arsenic contamination has sufficiently been discussed in terms of affected population and available resources with them. Thus, it was imperative to assess the developed adsorbent with regard to economic and environmental aspects. Therefore, to evaluate the sustainability, Eco scale and cost factor were also used.

2. Experimental Details

2.1. Chemicals and Reagents

All chemicals used in this study were of laboratory grade without further purification. All the glassware was thoroughly cleaned with lab wash (neutral) and washed thoroughly with tap water followed by rinsing with deionized

water and sterilized in hot air oven before use. Type II deionized water (resistivity =15.0 MΩ·cm) was used throughout the study. The laterite soil was collected from Kharagpur, India.

2.2. Procedure of synthesizing nano manganese (nMn) and nMn coated Laterite (Lt-nMn)

Synthesis of nano Mn was conducted by chemical reduction method using NaBH₄ (SRL Chemicals, India) as a reducing agent (Dada et al., 2017). In a typical synthesis, 0.05 M MnCl₂·4H₂O (Loba chemie, India) was prepared and transferred into three-necked round bottom flask. 0.2 M NaBH₄ was added dropwise under N₂ flow to the former solution. With the addition of NaBH₄ the colour of solution changed to brownish colour. Also, the hydrogen gas was evolving. The scheme of synthesis can be observed as per the following reaction (Eq.1).

The reaction mixture was further stirred for 3 h and allowed to age overnight. Later, it was filtered using cellulose nitrate membrane filter (0.22μ) and washed with ethanol and deionised water. The obtained solid product was oven dried at 60 °C for 5 h and kept in a desiccator for further application.

For synthesising the nMn coated laterite, first of all, collected laterite soil was washed with tap water and sun dried. Dried soil particles were crushed and sieved to obtain the particle size of 0.075 to 0.125 mm. Further, it was washed with a copious amount of deionized water and again sun dried. Finally, the soil particles were calcined at 750 °C for 1 h to remove primarily the organic impurities. In order to coat the nMn, calcined laterite particles were mixed with the manganese chloride solution and the synthesis process remained same as stated above for the nanoparticles. The amount of nMn coating was optimized as a function of As(III) removal.

2.3. Characterisation studies

The synthesized adsorbent particles were checked for their size, shape, surface area and purity by various techniques namely, Dynamic light scattering (DLS), Zeta potential, Field Emission Scanning Microscopy (FESEM), Atomic

force microscopy (AFM), X-ray diffraction (XRD), Energy Dispersive X-ray Spectroscopy (EDX), Fourier Transform Infrared Spectroscopy (FTIR) and Zero point charge analysis (pHzpc).

2.4. Sorption studies

Sorption studies for the removal of As(III) ions were performed in batch mode. Sodium (meta) arsenite (NaAsO_2) (Loba chemie, India) was used to make an As(III) stock solution with a concentration of 1000 mg/L. Working solution of desired concentration was prepared from the stock solution by the dilution method. Adsorption experiments were conducted as a function of affecting parameters such as contact time, initial concentration, dosage, pH, and temperature. The effect of the individual parameter was estimated by one variable at a time approach (OVAT). The variation in the range of parameters was observed as 10 - 2160 min for contact time; 100 - 1000 ppb for initial concentration; 0.25 - 4 g/L for dosage; 2 - 12 for pH; and 298 - 318K for the temperature. With the optimized value of parameters, isotherm and kinetic experiments were done to know the adsorption behavior and removal mechanism. In addition to it, oxidation study was also performed as a function of time. Removal efficiency in the presence of commonly found anions such as chloride, sulphate, carbonate, and phosphate were also tested for assessing its real performance in the field environment. The longevity of the adsorbent is always desirable for its field application and cost-effectiveness. Thus, a regeneration study was also performed for the prepared adsorbent. 50 mL solution containing adsorbent and adsorbate was shaken using orbital shaker (Rivotek, India) for a definite time interval. Thereafter, the solution was filtered using syringe filter (0.22 μ). The remaining As(III) concentration in the solution was measured using hydride generation technique of atomic absorption (HGAA) spectrophotometer (GBC Avanta-PM, Australia). During the batch study, adsorption capacity of Lt-nMn particles, and the removal efficiency were calculated using the following equations (Eq. 2 and 3):

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad \text{Eq. (2)}$$

$$R(\%) = \frac{(C_0 - C_e)100}{C_0} \quad \text{Eq. (3)}$$

Where, C_0 and C_e are the initial and equilibrium concentrations of As(III) in ppb. Q_e is the adsorption capacity at equilibrium in $\mu\text{g/g}$, V is the volume of the sample in litres and m is the weight (g) of Lt-nMn.

3. Results and Discussion

3.1. Structural analysis of the adsorbent

The results obtained from histogram analysis (Fig. 1) showed that the size majority of the particles is in the range of 14.91 - 118 nm. The moderate degree of stability of the manganese nano particles (n-Mn) in the aqueous solution was indicated by zeta potential value of -15.4 mV as shown in Fig. 2 (Madhavi et al., 2013). The morphological examination of the adsorbent using FESEM and EDX has been shown in Fig. 3 and Fig.4. The majority of the particles were spherical with aggregation. The size varied from 11 - 96 nm. Results of EDX analysis confirmed the purity of the adsorbent. Lt-nMn particles showed the presence of Fe, Al, and Si. 3-D topographic image obtained using AFM analysis showed hill-valley-like architecture due to agglomeration of the particles. The results were found consistent with the DLS and FESEM analysis (Fig. 5). The XRD pattern of the adsorbent presented in Fig. 6, shows the strong peaks at 2θ values of 40.09° , 41.48° , 42.87° , 50.01° , 74.12° , and 81.57° correspond to predominant diffraction peaks of zero valent Mn (ZVM) (Panda et al., 2019). Peaks at 2θ values of 24.5° and 38.7° showed the presence of goethite in the treated laterite sample. Besides, the peaks obtained at 2θ values of 28.91° , 32.42° , 38.38° , 58.54° ; and 47.9° , 53.7° correspond to Mn_3O_4 and weakly crystalline ferrihydrite respectively. The FTIR spectra of the adsorbent, before and after adsorption of As(III) are presented in Fig 7. Intense bands observed in the range of $400 - 650\text{ cm}^{-1}$ are ascribed to the Mn-O bending vibrations. The peaks obtained at 628 and 513 cm^{-1} correspond to the asymmetric bending vibrations of Mn-O in Mn_3O_4 and MnO_2 . The peak obtained in the range between $3300 - 3500\text{ cm}^{-1}$ and a weak band observed at 1625 cm^{-1} belong to the stretching and bending vibrations of O-H bonding related to the physically-sorbed water on the surface of the adsorbent. The characteristic peaks observed at 1408 cm^{-1} and 1002 cm^{-1} , were assigned to the bending vibrations of hydroxyl groups on the metal oxides. After As(III) adsorption on the adsorbent, the peaks at $\sim 1408\text{ cm}^{-1}$, 1625 cm^{-1} and 1002 cm^{-1} were observed to be slightly shifted upwards with decreased peak intensities. This primarily suggested that the surface hydroxyl group might be involved during the adsorption process. The peak observed at 820 cm^{-1} , which belongs to the stretching vibration of As(V)-O suggests the oxidation of As(III) to As(V) and presence of As(V) as surface complex, not as a precipitated solid phase (Zhang et al., 2007). The nMn particles had a surface area of $180\text{ m}^2/\text{g}$. While for Lt-nMn adsorbent, it was found as $79.6\text{ m}^2/\text{g}$.

Several recently reported studies on arsenic removal using nMn and laterite based adsorbents had been reported to contain lesser surface area values (Panda et al., 2019; Glocheux et al., 2013; Bui et al., 2017). The zero point charge (pHzpc) of the Lt-nMn based adsorbent was found to be 6.82 (Fig. 8), which confirms that the adsorbent was positively charged below pH 6.82.

3.2. Effect of nMn loading on As(III) removal

Quantity of nMn loading on laterite may affect the performance of the adsorbent in terms of As(III) removal efficiency. Therefore, the effect of nMn loading on laterite in different quantity was observed by varying the Mn concentration in the solution during loading operation from 0.01 M to 0.5 M. Control experiments with pure Mn and laterite adsorbent was also performed for comparison. Without nMn loading, the removal of As(III) was found as 96%. However, with the increase in the nMn loading up to 0.1 M, the removal efficiency kept on increasing (Fig. 9). With nMn concentration of more than 0.1 M, a constant trend in removal efficiency was observed. Thus, 0.1 M nMn was selected as the optimum concentration for loading during the preparation of Lt-nMn adsorbent. The calcination of laterite made it porous that helped in achieving the higher removal.

3.3 Parameters affecting adsorption

Contact time, initial arsenic concentration, adsorbent dose, pH, and temperature are the major parameters that may affect arsenic removal in any adsorption process.

3.3.1. Contact time

Contact time regulates the economic operation of any pilot-scale application. The effect of the contact time was evaluated with an initial As(III) concentration of 100 ppb, adsorbent dose of 1 g/L, and stirring speed of 150 rpm at neutral condition and at a temperature of 298 K. The contact time was varied in the range of 10 - 2160 min. From the results of the study (Fig 10), it can be seen that with increment in the reaction time from 10 min to 120 min, the arsenic removal efficiency improved from 94.7% to 99.8%. No notable change in the removal efficiency was found beyond

the contact time of 120 min due to saturation of the adsorption sites. Hence, the optimum contact time for further experiments was taken as 120 min. Lower C_e value in the initial phase of the experiment indicated the involvement of oxidation process, which was further analysed by lowering the contact time.

3.3.2. Effect of initial As(III) concentration

The effect of the initial As(III) concentration on removal efficiency was examined by varying concentration in the range of 100 - 1000 ppb at pH 7. Contact time and stirring speed were 120 min and 150 rpm respectively. The equilibrium arsenic concentration kept on increasing as the initial As(III) concentration increased as shown in Fig. 11. This observation suggested that with increase in the initial concentration, the number of surface sites got exhausted leading to incomplete removal of As(III) with a fixed dose of 1g/L. The uptake capacity with the rise of initial arsenic concentration, which was due to the driving force by high initial arsenic concentration to overpower all the mass transfer barriers between the solid and aqueous phases of the contaminant (Ghosh et al., 2019). The percentage removal reached a constant value at the initial concentration of 800 ppb. No significant change in the removal efficiency was seen with further increment in the initial As(III) concentration. Optimum initial arsenic concentration was, therefore, selected as 800 ppb. It is important to note that with a low initial As(III) concentration of 100 ppb, the performance of Lt-nMn adsorbent was very satisfactory, as less than 10 ppb As(total) concentration was achieved after treatment. In natural groundwater, the As(III) concentration is generally less than 800 ppb. Thus, the satisfactory performance of the adsorbent even with very less initial arsenic concentration demonstrated its compatibility to decrease the arsenic concentration below WHO permissible limit of 10 ppb for arsenic in drinking water.

3.3.3. Adsorbent Dose

The economy of any treatment system depends on the use of optimized quantity of adsorbent dose. In order to observe the response of the adsorbent dose, experiments were carried out by varying the dose from 0.2 - 4 g/L at pH 7. Samples with initial As(III) concentration of 800 ppb were agitated for 120 min at 150 rpm. The results shown in Fig. 12 revealed that removal efficiency rapidly increased from 81.8 % to 97.7 % when the dose was escalated from 0.25 g/L

to 1.5 g/L. On further increment of the adsorbent dose, no substantial change was observed. Therefore, for further studies an adsorbent dose of 1.5g/L was selected as optimum.

3.3.4. *Effect of pH*

pH controls the speciation of arsenic [arsenite As(III) and arsenate As(V)] as well as the charge developed at the surface of the adsorbent, thus regulates the feasibility of the adsorption process (Jamal Uddin and Jeong, 2020). The response of varying pH on the removal of As(III) by Lt-nMn adsorbent was examined over a wide pH range of 2 - 12. Initial As(III) concentration was 800 ppb with an adsorbent dose of 1.5 g/L. Weak dependence of As(III) removal on pH was observed in the pH range 2 - 8 as shown in Fig.13. Around 95% arsenic removal was obtained in this pH range. However, with the pH value more than 8, the percentage of As(III) removal significantly reduced. As(III) was getting oxidized to As(V) during adsorption reaction as discussed earlier. As(V) occurs as an anionic species in the pH range of ~ 2 - 14 (Ghimire et al., 2003). As the pH_{Zpc} value of the adsorbent is 6.82, the adsorbent surface will be positively charged and will adsorb more anions below pH 6.82. At pH value > pH_{Zpc}, the electrostatic repulsion between the negatively charged adsorbent surface and As(V) led to significantly less removal of arsenic. At higher pH, the excess concentration of OH⁻ ion in the solution might impart a competitive effect with arsenic for adsorption on the surface sites of Lt-nMn (Pal et al., 2015). Thus, it can be said that the optimum pH range for As(III) removal is 2 - 8. This wide range of working pH falls in the natural groundwater pH (~6.8) and indicated to be beneficial in large-scale application without any pre-treatment to adjust the pH.

3.3.5. *Temperature*

The applicability of a developed treatment system is largely influenced by its robustness to work in different temperature conditions. The effect of temperature on As(III) removal was therefore, investigated with a wide variation in temperature and As(III) concentration ranging from 298K to 318K and 100 - 800 ppb respectively. Contact time of 120 min, stirring speed of 150 ppm and neutral pH condition were maintained throughout the experiments. Adsorbent dose of 1.5 g/L was added. It is evident from Fig. 14 that as the temperature was raised, the removal efficiency of As(III) kept on decreasing for the entire range of concentrations studied. The highest removal efficiency was obtained

at 298K. Furthermore, the results of this study suggested that low (natural) temperature condition is favorable for carrying out the adsorption process, leading to no requirement of any extra energy input, which in turn reduces the cost of treatment. It is important to note that 97.4% removal was still achieved with the highest escalated temperature of 318K. Thus, it can be said that the adsorbent proves to work efficiently in a wide range of temperatures.

3.4. Adsorption isotherm

The adsorbate molecules remain distributed between the solid and liquid phase at equilibrium condition [22]. Adsorption isotherm is a mathematical tool that helps to understand the adsorption equilibrium. In the present study, Langmuir and Freundlich, the two extensively used isotherm models, have been applied for better understanding the interaction between the adsorbent and adsorbate. Experiments were performed at three different temperatures of 298 K, 308K, and 318K with the initial As(III) concentration varying from 100 ppb to 800 ppb. A fixed adsorbent dose of 1.5g/L was added.

3.4.1. Langmuir isotherm

Langmuir isotherm is used for single solute adsorption system. Adsorption is assumed to be monolayer on to the adsorption sites posing equal adsorption energy (Prabhakar and Samadder, 2020). The non-linear expression of this adsorption model is shown in Eq. (4) (Lata et al., 2019).

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad \text{Eq. (4)}$$

Where Q_e ($\mu\text{g/g}$) represents adsorption capacity at equilibrium concentration C_e (ppb). Q_m is the maximum monolayer adsorption capacity and K_L ($\text{L}/\mu\text{g}$) symbolizes the Langmuir constant related to the energy of sorption. The values of Q_m and K_L were calculated from the slope and intercept of plot of C_e and Q_e respectively (Fig. 15). Table 1 presents the calculated values of isotherm parameters. The value of K_L was calculated to be 0.050 $\text{L}/\mu\text{g}$, 0.040 $\text{L}/\mu\text{g}$, and 0.033 $\text{L}/\mu\text{g}$ at temperatures 298 K, 308 K, and 318 K respectively. Higher K_L values at lower temperatures indicate that the

adsorption is favored in lower temperatures. As evident from Table 1, the maximum adsorption capacity was 1376.88 $\mu\text{g/g}$, 1240.06 $\mu\text{g/g}$, and 1184.67 $\mu\text{g/g}$ at 298 K, 308 K, and 318 K respectively.

3.4.2. Freundlich isotherm

Freundlich isotherm model is generally applied for heterogeneous adsorption characteristics and sorption sites having non-uniform energies of sorption. Eq. (5) demonstrates the non-linear form of this isotherm model (Rauf et al., 2019).

$$Q_e = K_f C_e^{1/n} \quad \text{Eq. (5)}$$

Where, C_e (ppb) and Q_e ($\mu\text{g/g}$) have the same meaning as stated earlier. $K_f \{(\mu\text{g/g})/(\mu\text{g/L})^{1/n}\}$ and n correspond to Freundlich constants, and are related to adsorption capacity and adsorption intensity respectively. Fig. 16 was used to obtain these parameters and is listed in Table 1. The calculated values of K_f were found to be 80.10, 64.997, and 57.074 at three different temperatures of 298 K, 308 K, and 318 K respectively. The declined K_f values with the rise in the temperature indicated that low-temperature condition is preferable for As(III) adsorption using Lt-nMn adsorbent. The calculated values of $1/n$ at 298 K, 308 K, and 318 K were 0.763, 0.735, and 0.724 respectively. Values of $1/n$ lesser than 1 showed that the adsorption process is favourable (Rauf et al., 2019).

Furthermore, the fitness of models was evaluated not only as a function of R^2 but also considered error function chi-square (χ^2) which is represented by Eq. (6).

$$\chi^2 = \sum_{i=1}^n \frac{(q_{\text{ecalc}} - q_{\text{eexp}})^2}{q_{\text{eexp}}} \quad \text{Eq. (6)}$$

Although the R^2 values for both the models were found very similar. However, the χ^2 values were able to distinguish the model applicability. Langmuir isotherm model yielded lower χ^2 values than the Freundlich isotherm. This suggested the applicability of the Langmuir equation for the present study. Langmuir maximum adsorption capacity

of Lt-nMn adsorbent outperformed several other adsorbents such as Fe (III) – Sn (IV) mixed binary oxide – coated sand, manganese and iron oxide pillared clays, α -MnO₂ nanowires, alpha nano alumina, iron impregnated banana pith biochar, silica based catalytic media and laterite soil which were applied for As(III) removal (Table 2).

3.5. Kinetic studies

The time required by the adsorbent to uptake the contaminant to reach equilibrium is explained by adsorption kinetics. Kinetic studies also facilitate useful information about the mechanism of adsorption. Experiments were performed with initial As(III) concentration of 800 ppb, adsorbent dose of 1.5 g/L, and a wide range of temperature (298 K - 318 K). Samples were shaken for different time intervals (5 min - 120 min) at 150 rpm and at neutral pH.

3.5.1. Pseudo-first order kinetic model

Eq. (7) exhibits the non- linear form of the pseudo-first-order kinetic model (Ho and McKay,1998) .

$$Q_t = Q_e (1 - e^{-k_1 t}) \quad \text{Eq. (7)}$$

Where, Q_e and Q_t (both in $\mu\text{g/g}$) depict the amount of arsenic adsorbed at equilibrium and at any time t respectively. Theoretical adsorption capacity and pseudo-first-order rate constant (k_1) were obtained from the slope and intercept respectively of the plot of Q_t vs. time (t) as shown in Fig. 17. From the rate constants shown in Table 3, it can be seen that k_1 varied from 0.809 min^{-1} to 0.684 min^{-1} with the increase in the temperature from 298 to 318 K. The lower R^2 value obtained in this model suggested that pseudo-first-order model could not be applied as kinetic model for the present study.

3.5.2. Pseudo-second-order kinetic model

The data obtained during the kinetic experiments were tested using pseudo-second-order kinetic model as shown by Eq. (8).

338

339

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad \text{Eq. (8)}$$

340

341 Where, Q_e and Q_t bear a similar meaning as stated before. K_2 is the pseudo-second order rate constant and obtained
342 from the plot of Q_t vs. t [Fig. 18]. The obtained R^2 value was found satisfactory as can be seen from Table 2. Hence,
343 pseudo-second order kinetic model did explain the adsorption kinetic for the present study. In order to identify the rate
344 limiting step in the adsorption process, intra-particle and liquid film diffusion model was employed.

345

346 3.5.3 Intra-particle diffusion

347

348 The assumptions of this model are, the adsorbate travels to the pore of the adsorbent after being primarily surface
349 adsorbed and adsorption capacity is directly proportional to $t^{0.5}$. The mathematical expression of this model is given
350 by Eq. (9) (Morris and Weber, 1963).

351

$$Q_t = k_{id} t^{0.5} + C \quad \text{Eq. (9)}$$

353

354 Where, k_{id} and C denote intra-particle diffusion rate constant and intercept of the graph respectively as shown in
355 Fig. 19. It showed that the straight line did not cross through the origin and a multi-segmented plot was obtained,
356 which suggests that intra-particle diffusion is not a rate-limiting step for the current study. The high value obtained
357 for the intercept at three different temperatures is a preliminary indication of the role of the boundary layer for the
358 adsorption process (Khan et al., 2013).

359

360 3.5.4. Liquid film diffusion

361

362 As the intra particle diffusion model did not clearly explain the rate limiting step for the current study, liquid film
363 diffusion model was employed to the experimental data of the kinetic study. The model is expressed by Eq. (10)
364 (Weber and Chakravorti, 1974).

$$\ln(1-f) = -k_{fd}t \quad \text{Eq. (10)}$$

Where, the fractional achievement of equilibrium is denoted by $f = Q_t/Q_e$ and k_{fd} is the rate constant of liquid film diffusion. A straight line was produced at all four temperatures as can be seen from the plot of $\ln(1-f)$ vs. t [Fig. 20]. At 298 K, 318 K, and 308 K the k_{fd} values were -0.011, -0.029, and -0.030 respectively. The higher R^2 (0.95 to 0.89) and lower intercepts (-3.4 to -3.23) obtained in this model than that of intra-particle diffusion, suggested that the formation of a film of oxides of Mn and Fe on the adsorbent surface might control the adsorption kinetics for the present study (Table 4).

3.6. Thermodynamic studies

Temperature related experimental data were further analyzed to calculate different thermodynamic parameters such as standard free energy (ΔG°), standard entropy (ΔH°) and standard enthalpy (ΔS°) for a better understanding of the adsorption mechanism. Different parameters of thermodynamic study have been shown in Eq. (11) – (13) (Nassar et al., 2017).

$$\Delta G^\circ = -RT \ln K_c \quad \text{Eq. (11)}$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \text{Eq. (12)}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad \text{Eq. (13)}$$

Where, R denotes the universal gas constant (kJ/mol.K), T (K) is the temperature, K_c represents solute distribution coefficient and was obtained from the ratio of Q_t/C_e . The slope and intercept of the plot between $\ln K_c$ vs. $1/T$ (Fig. 21) yielded the value of ΔH° and ΔS° respectively and presented in Table 5. Standard enthalpy (ΔH°) and entropy values (ΔS°) were calculated as -21.27 kJ/mol and -0.04 kJ/mol.K. The ΔH° value less than 40 kJ/mol suggests that the adsorption process might be physio-sorption. Negative ΔS° value indicated that the randomness of the solute [As(III)]

decreased in the solution as the concentration of the adsorbate increased on the surface of the adsorbent. At three different temperatures of 298 K, 318 K, and 308 K, the standard free energy (ΔG°) was found to be -9.34 kJ/mol, -8.94 kJ/mol, and -8.54 kJ/mol respectively. These negative values of ΔG° at all three temperatures further exhibited the spontaneous and favorable nature of adsorption. The declined value of ΔG° with the rise in the temperature further showed that the adsorption process is less likely to occur at higher temperatures. Furthermore, in the present study, ΔG° was found to be in the range of 0 to -20 kJ/mol, which made the process to be physio-sorption (Nassar and Khatab, 2016).

3.7. Investigation of possible oxidation of As(III) to As(V) by Lt-nMn particles

Oxidation of As(III) was evaluated with an initial As(III) concentration of 100 ppb. 1.5 g/L adsorbent dose was added and samples were shaken for a different time interval ranging from 1 to 10 min. Fig. 22 shows that the concentration of As(III) kept on decreasing as the reaction progressed, whereas, As(V) concentration was increasing. It was observed that till 10 min of contact time, As(V) concentration increased. Interestingly, after 7 min, the total arsenic concentration started decreasing, which was the mark of the initiation of adsorption process. The oxidation of As(III) into As(V) can, therefore, be due to the formation of oxides of manganese on the adsorbent surface, mainly MnO_2 . The observed characteristic band for As(V)-O during the FTIR study of the adsorbent sample after adsorption also supported this result. A similar observation was also reported in the previous studies (Lou et al., 2017).

3.8. Effect of coexisting ions

Anions such as phosphate, chloride, sulphate, and carbonate are generally found to be present in groundwater and reported to influence the arsenic removal efficiency due to their competitive effects on the binding sites of the adsorbent (Maiti et al., 2012). The effects of these competing coexisted ions were evaluated at a high concentration (2000 ppb) of these anions separately. An optimum adsorbent dose of 1.5 g/L was added to 800 ppb initial As(III) concentration at pH 7. From the results of this study shown in Fig. 23, it was observed that the chloride and carbonate did not noticeably affect the removal efficiency of the adsorbent. Whereas, in the presence of sulphate and phosphate, As(III) removal efficiency was reduced by 1% and 1.7% respectively. The slight reduction in the removal efficiency

in the presence of these co-ions suggested that the oxidation of As(III) into As(V) gave a preferential selectivity to arsenic adsorption over phosphate, indicating higher affinity of the Lt-nMn towards As(V) species. Furthermore, it can be said that Lt-nMn has a good potential in treating arsenic containing groundwater with a high concentration of coexisting anions.

3.9. Regeneration of Lt-nMn adsorbent

Reusability of any adsorbent directly controls the economic feasibility of that particular treatment technology. Thus, a regeneration study of the adsorbent was done to establish its reusing capability and economic feasibility of the treatment system. The adsorbent was regenerated by raising the pH above the zero point charge of the adsorbent ($pH_{zpc} = 6.8$) using 0.1 N NaOH. Above pH_{zpc} , the negatively charged adsorbent surface desorbed As(III) oxyanion. Four adsorption-desorption cycles were carried out with 800 ppb initial As(III) concentration (Fig. 24). Only 3% reduction in the removal efficiency was observed at the end of 4th cycle, which suggests that the adsorbent has a very high reusable capacity that may reduce the treatment cost to a great extent.

4.0. Eco-Scale and cost analysis for the synthesis of Lt-nMn adsorbent

Table 5a shows eco-scale analysis for the synthesis of Lt-nMn adsorbent for arsenic removal. The penalty points for each material were allocated based on the safety, cost, and energy requirement (Medina-Ramirez et al., 2019). In the present study, eco-scale value for the method of synthesis of Lt-nMn particles was found as 86%. Generally, the eco-scale value greater than 75% is considered as a green process. Additionally, the environment factor (E factor) and water intensity were calculated as 0.008 and 34.37 respectively.

$E \text{ factor} = [\text{kg (raw materials)} - \text{kg (desired product)}] / \text{kg (total product including water)}$ Eq.(14)

$\text{Water intensity (Wp)} = (\text{mass of all water used} / \text{mass of product}) \text{ kg/kg product}$ Eq. (15)

These indices cumulatively suggested the process to be a sustainable and greener. The method seems to be a water positive, since, for every one litre of water consumed for synthesis, nearly 220 L of water can be treated. The approximate cost of synthesis of the adsorbent was calculated by considering the prices of the raw materials used

during its production. The cost of production of Lt-nMn adsorbent was 0.0958 USD/g (Table 5b). This showed that the synthesis process is feasible from economic point of view.

4.1. Amount estimation study using adsorber design analysis

Apart from sustainability analysis, it is equally important to quantify the required amount of Lt-nMn particles for treating the known volume of arsenic-contaminated water. Design of single stage batch adsorber by mass balance approach, can help in estimation of the amount. The results of isotherm adsorption experiment were applied to the following equations (Eq.16) to find the required dosage (Prabhakar and Samadder, 2020).

$$\frac{M}{V} = \frac{C_1 - C_e}{Q_e} \quad \text{Eq. (16)}$$

The Q_e value in Eq. 16 can be found using the Langmuir isotherm, as this was the governing isotherm model in the present study. Therefore, Eq. 16 can be rewritten as,

$$\frac{M}{V} = \frac{C_1 - C_e}{\frac{Q_m K_L C_e}{1 + K_L C_e}} \quad \text{Eq. (17)}$$

Where the C_1 and C_e are the initial and desired equilibrium arsenic concentration. If the values of C_1 , C_e , Q_e , and V are known, then with the help of Eq. (17), mass of Lt-nMn can easily be calculated. For a hypothetical situation, the equilibrium concentration was fixed at 5 ppb for different concentrations ranging from 100 to 500 ppb. The range of chosen concentration mimics the natural arsenic concentration found in this region. Fig. 25 shows the calculated amount of Lt-nMn particles for different volumes of water to be treated. For treating the 1000 L water having 200 ppb concentration, approximately 0.70 kg of Lt-nMn is required. Out of this amount, much of the portion consists of laterite soil particles. Also, if regeneration efficiency is taken into consideration then nearly 4 times higher volume of water can be treated with the same amount of Lt-nMn particles.

5. Conclusions

This study reported the efficient and cost-effective method for the synthesis of nano Mn coated laterite particles, that were applied for As(III) removal from groundwater. Laterite soil as a base material for nano Mn coating not only provided the synergism for removal but also provided a way to think beyond the sole use of nano materials for removal processes. Coating of nMn was optimised as a function of As(III) removal efficiency. With pure nMn and laterite particles, less removal was observed. The calcination process removed the organic impurities and thus hardness and porosity were improved. This eventually prevented the disintegration and adhesion in water. Characterisation studies using FESEM analysis revealed that synthesized nMn particles were spherical and of nano size range. EDX analysis further confirmed the purity of nMn. Surface area of Lt-nMn was found lower as compared to nMn which further assured that coating was successfully achieved. Results of adsorption studies reflected that the up to 700 ppb of initial As(III) concentration, remaining concentration in the solution was brought down below the 10 ppb mark. Oxidation of As(III) species facilitated the smooth removal arsenic ions in the form of As(V). The removal was insignificantly affected till pH 7. Adsorption isotherm was clarified satisfactorily by Langmuir isotherm with a maximum monolayer adsorption capacity of 1376.882 $\mu\text{g/g}$ at 298 K. Isotherm and thermodynamic studies indicated an exothermic nature of adsorption. Adsorption was less likely to be affected by the presence of commonly found anions in the groundwater. Furthermore, the sustainability studies confirmed that the Lt-nMn had very less potential to cause any harm to the environment.

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500 **Consent to publish**

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502 **Authors' contributions**

503 **Conceptualization:** Roshan Prabhakar; **Methodology:** Roshan Prabhakar, Somaparna Ghosh, Ali; **Formal analysis**
504 **and investigation:** Somaparna Ghosh, Ali; **Writing - original draft preparation:** Roshan Prabhakar, Somaparna
505 Ghosh; **Writing - review and editing:** Roshan Prabhakar, Sukha Ranjan Samadder; **Funding acquisition:** Sukha
506 Ranjan Samadder; **Resources:** Sukha Ranjan Samadder; **Supervision:** Sukha Ranjan Samadder, Roshan Prabhakar

507 **Competing interests**

508 The authors declare that they have no competing interests.

509 **Availability of data and materials**

510 All data generated or analysed during this study are included in this manuscript.

511

512 **References**

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Table 1: Values of the adsorption isotherm parameters for As(III) using Lt-nMn adsorbent

S. No	Isotherm models	Temperature (K)		
		298	308	318
1.	Langmuir isotherm			
	Q_m ($\mu\text{g/g}$)	1376.882	1240.061	1184.671
	K_L ($\text{L}/\mu\text{g}$)	0.050	0.040	0.033
	R^2	0.996	0.993	0.993
	χ^2	2.02	6.60	8.40
2.	Freundlich isotherm			
	$K_f \{(\mu\text{g/g})/(\mu\text{g/L})^{1/n}\}$	80.101	64.997	57.074
	$1/n$	0.763	0.735	0.724
	R^2	0.993	0.998	0.990
	χ^2	3.89	7.31	9.63

Table 2: Adsorption capacities of various adsorbents used for As (III) removal

Adsorbent	Maximum adsorption capacity ($\mu\text{g/g}$)	Reference
Fe (III) – Sn (IV) mixed binary oxide – coated sand	82.64	Chaudhary et al., (2016)
Manganese oxide pillared clays	25.77	Mishra and Mahato, (2016)
Iron oxide pillared clays	17.57	Mishra and Mahato, (2016)
α -MnO ₂ Nanowires	1012	Wei et al.,(2017)
Alpha nano alumina	500	Prabhakar and Samadder, (2018)
Iron impregnated banana pith biochar	120.91	Lata et al., (2019)
silica based catalytic media	315	Aremu et al.,(2019)
Laterite soil	602	Nguyen et al., (2020)
Lt-nMN particles	1376.88	<i>Present study</i>

Table 3: Values of the kinetic parameters for As(III) using Lt-nMn adsorbent

S. No	Applied Kinetic Models	Temperature (K)		
		298	308	318
1.	Pseudo-first-order			
	Q_m ($\mu\text{g/g}$)	517.530	515.293	513.124
	k_1	0.809	0.862	0.684
	R^2	0.60	0.48	0.72
	χ^2	0.060	0.064	0.066
2.	Pseudo-second-order			
	Q_m ($\mu\text{g/g}$)	520.564	518.118	517.867
	k_2	0.140	0.124	0.236
	R^2	0.89	0.82	0.96
	χ^2	0.002	0.014	0.019

Table 4: Intra particle and liquid film diffusion parameters for As(III) adsorption using Lt-nMn adsorbent

S. No.	Temperature (K)	Intra particle diffusion			Liquid film diffusion		
		$K_{id} (\mu\text{g.g}^{-1}.\text{min}^{-1})$	Intercept	R^2	$K_{fd} (\text{g. } \mu\text{g}^{-1})$	Intercept	R^2
1.	298	10.11	506.37	0.93	-0.011	-3.40	0.95
2.	308	9.39	504.27	0.96	-0.029	-3.47	0.98
3.	318	9.36	496.65	0.81	-0.030	-3.23	0.89

Table 5: Thermodynamic parameters of the adsorption process for As(III) removal using Lt-nMn adsorbent

S. No.	Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol. K)
1.	298	-9.34	-21.27	-0.040
2.	308	-8.94		
3.	318	-8.54		

Table 6: Sustainability assessment for the synthesis of Lt-nMn adsorbent particles (A) Eco-Scale and (B) Cost

(B) Eco-Scale

Parameter	Amount	Penalty Points (PP)
Laterite	<10 g	0
MnCl ₂ .4H ₂ O	< 10 g	1
NaBH ₄	< 10 g	2
Ethanol	10-100 ml	4
Waste	< 1 g	1
Common setup	----	0
Inert Gas atmosphere	----	1
Room temperature < 24 h	-----	1
Adding solvent	----	0
Heating > 1h	---	3
AAS	---	1
Total Penalty Points (TPP)		14
Eco-Scale		<i>(100-14)= 86</i>

(B) Cost

Reagent	Amount (g)	Amount (ml)	Price (USD)	Price (USD/g)
Laterite	1	----	0	0
MnCl ₂ .4H ₂ O	0.49	----	0.01	0.0204
NaBH ₄	0.60	----	0.08	0.133
Water	55	55	0	0
Total Cost				0.1534
Lt-nMn adsorbent	1.6	---		
Cost of Lt-nMn adsorbent (USD/g)	<i>0.0958</i>

Fig. 1: Dynamic light scattering (DLS) analysis of Mn nanoparticles

Fig. 2: Zeta potential analysis of Mn nanoparticles

Fig. 3: FESEM and EDX analysis of Mn nanoparticles

Fig. 4: FESEM and EDX analysis of Lt-nMn adsorbent particles

Fig. 5: AFM analysis of Mn nanoparticles

Fig. 6: XRD pattern of Lt-nMn adsorbent particles

Fig. 7: FTIR spectra of synthesized Lt-nMn particles (a) before adsorption and (b) after adsorption of As(III)

Fig. 8: Zero point charge (pH_{ZPC}) of Lt-nMn adsorbent particles

Fig. 9: Effect of nMn loading on As(III) removal

Fig. 10: Effect of contact time on As(III) removal (experimental conditions: i.c – 100 ppb, dose – 1 g/L, pH - 7 ± 0.2 , temp: 298 K, contact time: 10 - 2160 min, stirring speed – 150 rpm)

Fig. 11: Effect of initial concentration on As(III) removal [experimental conditions: i.c – 100 - 1000 ppb, dose – 1 g/L, pH - 7 ± 0.2 , temp: 298 K, contact time – 120 min, stirring speed – 150 rpm]

Fig. 12: Effect of adsorbent dose on As(III) removal [experimental conditions: i.c – 800 ppb As (III), dose: 0.25 – 4 g/L, pH - 7 ± 0.2 , temp: 298 K, contact time – 120 min, stirring speed – 150 rpm]

Fig. 13: Effect of pH on As(III) removal [experimental conditions: i.c – 800 ppb A, dose – 1.5 g/L, pH – 2- 12, temp: 298 K, contact time – 120 min, stirring speed – 150 rpm]

Fig. 14: Effect of temperature on As(III) removal (experimental conditions: i.c – 100-800 ppb, dose – 1.5 g/L, pH - 7 ± 0.2 , temp: 298 – 318 K, contact time – 120 min, stirring speed – 150 rpm)

Fig. 15: Langmuir isotherm model for As(III) adsorption (experimental conditions: i.e – 100- 800 ppb, dose - 1.5 g/L, pH - 7 ± 0.2 , temp. - 298 – 318 K, contact time – 120 min, stirring speed – 150 rpm)

Fig. 16: Freundlich isotherm model for As(III) adsorption (experimental conditions: i.c – 100- 800 ppb, dose - 1.5 g/L, pH - 7 ± 0.2 , temp. - 298 – 318 K, contact time – 120 min, stirring speed – 150 rpm)

Fig. 17: Pseudo – first – order kinetic model (experimental conditions: i.c – 800 ppb, dose – 1.5 g/L, pH - 7 ± 0.2 , temp: 298-318 K, contact time – 5 - 120 min, stirring speed – 150 rpm)

Fig. 18: Pseudo – second – order kinetic model (experimental conditions: i.c – 800 ppb, dose – 1.5 g/L, pH - 7 ± 0.2 , temp: 298-318 K, contact time – 5 - 120 min, stirring speed – 150 rpm)

Fig. 19: Intra particle diffusion kinetic model (experimental conditions: i.c – 800 ppb, dose – 1.5 g/L, pH - 7 ± 0.2 , temp: 298-318 K, contact time – 5 - 120 min, stirring speed – 150 rpm)

Fig. 20: Liquid film kinetic model (experimental conditions: i.c – 800 ppb, dose – 1.5 g/L, pH - 7 ± 0.2 , temp: 298-318 K, contact time – 5 - 120 min, stirring speed – 150 rpm)

Fig. 21: Thermodynamic studies for determination of Gibb's free energy (ΔG°), change of standard enthalpy (ΔH°) and change of standard entropy (ΔS°) for As (III) removal

Fig. 22: Oxidation of As(III) to As(V) during arsenic removal using Lt-nMn adsorbent (experimental conditions: i.c= 100 ppb As(III); dose = 1.5 g/L; pH = 7 $\pm$ 0.2; Temperature = 298 K)

Fig. 23: Effect of competing anions on As(III) adsorption (Experimental conditions: i.c – 800 ppb, competing ions conc. – 2000 ppb, adsorbent dose – 1.5 g/L, pH – 7 ± 0.2 , temp. – 298 K, stirring speed – 150 rpm)

Fig. 24: Regeneration study of Lt-nMn adsorbent (Experimental conditions: i.c of As (III) - 800 ppb, normality of NaOH - 0.1 N, adsorbent dose – 1.5 g/L, contact time - 120 min, stirring speed - 150 rpm)

Fig. 25: Amount of Lt-nMn required for treating different volume with different arsenic concentrations