L-Histidine immobilized montmorillonite for As(III) adsorption and statistical verification of data by PDF, AICcorrected and AADR models

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Abstract
L-Histidine immobilized montmorillonite is prepared and used as an adsorbent for removal of As(III) from aqueous solutions. The L-Histidine immobilized montmorillonite is characterized by FTIR, XRD, TGA and PZC techniques that confirmed the successful insertion of Histidine into interlayer of montmorillonite structure. The various parameters such as pH, reaction time, temperature, concentration of As(III) and adsorbent dosage are optimized to obtain maximum As(III) adsorption. It is observed that usually the removal of As(III) is increased with increasing the amount of adsorbent, contact time, temperature and till pH 6. The results showed that all these adsorption parameters greatly influenced the adsorption process. The various adsorption isotherm models including Langmuir, Freundlich, Temkin and Dubinin-Radishkevich (DR) as well as kinetics models are applied to the adsorption data. The Langmuir isotherm and pseudo-second order kinetics model are well-fitted to the adsorption data. Further, the probability distribution function (PDF) is applied that verified the adsorption data well while the Akaike's Information Criterion (AICcorrected) and Absolute Average Relative Deviation (AARD) statistical models supported the best fit adsorption isotherms. The PDF model have provided a good statistical identification of adsorption parameters, adsorption rates and maxima whereas AICcorrected and AARD models revealed the well-fitting of Langmuir adsorption isotherm model in correlating the equilibrium data. Thermodynamic parameters (ΔH, ΔS, ΔG) proved the endothermic and spontaneous nature of adsorption process along with entropical changes occurring at solid-solution interface. The results showed that L-Histidine immobilized montmorillonite is an excellent material for As(III) adsorption with maximum adsorption capacity of 87.7 mg g⁻¹.

Keywords Montmorillonite · L-Histidine · As (III) · Adsorption isotherm · Kinetic models · Probability distribution function

Introduction
Arsenic is naturally occurring in earth crust as well as in underground and surface water due to natural weathering and anthropogenic activities (Martinson and Reddy 2009). It exists in various oxidation forms (−3, 0, +3, +5). From these oxidation states, arsenic has been detected in As(III) and As(V) stable oxidation states (Bessaies et al. 2020). These both forms of Arsenic are toxic but As(III) is comparatively sixty times more toxic than As(V) (Mohan and Pittman Jr 2007, Singh et al. 2015). The permissible level of As(III) in drinking water is 5 × 10⁻⁵ to 1 × 10⁻⁵ g.L⁻¹ according to recommendation of World Health Organization (WHO) (Basha, Selvi et al. 2009). The presence of As(III) above this limit causes serious health issues like skin and lung cancers, anemia, keratosis, hyperpigmentation, liver fibroses and neurological disorders (Mondal et al. 2020).

The number of methods available for removal of As(III) from water and waste water solutions which include reverse osmosis, chemical coagulation, chemical precipitation, electrochemical methods, membrane filtration, ion exchange process (Arahman et al. 2018, Khan, Sherazi et al. 2018,
Sherazi et al. 2022). Among all the above described techniques, adsorption is more efficient and ideal technique for removal of As(III) from aqueous solution. A number of adsorbents have been practically used for the removal of As(III) which include nanofibers, carbon nanotubes, oxide and hydroxide nanoparticles and biomasses ion exchange resins (Razzaq, Shah et al 2020). The use of these adsorbents for the removal of As(III) from aqueous solution is not economical and feasible and also degradation of these adsorbents produces a large amount of sludge and secondary pollutants in water.

The selection of natural clays, minerals and rocks such as bentonite, montmorillonite, kaolin, zeolite, calcite, dolomite and diatomite as adsorbents can be considered a best option due to several advantages of high thermal stability, wide availability and excellent adsorption potential, low cost and green nature (Jiang et al. 2002). In addition, the surface and adsorption characteristics of these adsorbents can be easily modified using different surface modifying agents (Zhu et al. 2017).

The area of interest in current study was to improve the adsorption properties of Montmorillonite clay by using surface modifier L-Histidine, a biological material. Recently, Tyrosine immobilized montmorillonite was employed as an adsorbent for removal of inorganic metal ions, Pb\(^{2+}\) and Cu\(^{2+}\) and results proved an excellent performance of adsorbent for metal ion decontamination. (Chu et al. 2019). Similarly, L-Cysteine modified montmorillonite alginate nanocomposite was used as an adsorbent for the removal of Ni\(^{2+}\), Pb\(^{2+}\) and Cu\(^{2+}\) and satisfactory results were reported (Mittal et al. 2016).

L-Histidine is a type of basic amino acid having positive charge under weekly acidic conditions which can easily form complex with metal ions due to good chelating capability (Palit and Moulik 2001, Bakatula, Cukrowska et al. 2014). The surface modification of montmorillonite with L-Histidine can result in synthesis of an ideal and economical adsorbent with improved adsorption properties for decontamination of many cationic pollutants in water bodies. The current study, thus investigates the L-Histidine immobilized montmorillonite (His-MMt) adsorbent for the removal of As(III) from aqueous solution and it is necessary to mention that it is the first report regarding its surface and Adsorption characteristics for As(III) removal. In addition, the objective of the current investigation is also to evaluate the adsorption data and suitability of different adsorption isotherm models using different statistical models like probability distribution function (PDF), Akaike’s information criterion (AIC corrected) and Arithmetic Average Relative Deviation (AARD). The statistical approach for evaluation of adsorption data and well-fitting of adsorption isotherm models is mandatory to identify the As (III) adsorption plateau and maxima, adsorption rates and mechanism.

### Material and reagents

In this work, all chemicals used were of high purity analytical grade and used without any further purification. Na-Montmorillonite (Na-MMt), Arsenic trioxide (As\(_2\)O\(_3\)), Potassium Iodide (KI), Potassium Iodate (KIO\(_3\)), Hydrochloric acid (HCl), Sodium hydroxide (NaOH), Sodium Chloride (NaCl), L-Histidine (C\(_6\)H\(_9\)N\(_3\)O\(_2\)) and Methylene Blue (C\(_{16}\)H\(_{18}\)CIN\(_3\)S) of analytical grade were purchased from Daejung, South Korea. All the experiments were carried out using ultrapure distilled water. The standard stock solution of As(III) was prepared by dissolving 1.320 g of As\(_2\)O\(_3\) in 20 mL of 1 M NaOH. In this solution, 50 mL of 0.5 M HCl solution was added and the volume was adjusted to 1000 mL by deionized water. The working solutions of different concentration of As(III) were prepared by dilution of stock solution. The solutions of HCl (1 M), NaOH(1 M), 2%KI and 2% KIO\(_3\) were prepared. The 1 mg/L solution of methylene blue was prepared by dissolving 1 mg of methylene blue in 1L of deionized water.

### Arsenic (III) determination

A series of standard solutions containing 1–10 mg L\(^{-1}\) of As(III) were poured into a series of 50 mL calibrated flask then 4 mL of 1 mg/L methylene blue were added having solution pH was 4. After that 2 mL of 2% KI and mL of 2% KIO\(_3\) were added respectively and shaken slowly. The absorbance of solution was measured at \(\lambda_{\text{max}}\) of 353 nm using UV–Visible spectrophotometer as reported in literature (Shah, Fahad et al. 2021).

### Adsorption experiment

The adsorption parameters were studied by applying different experimental conditions to find out the optimum range for excellent adsorption efficiency of adsorbent. For kinetic study, 10 mg of His-MMt adsorbent was added in 100 mL of 1 mg.L\(^{-1}\) As(III) solution. The samples for determination of As(III) were collected after different time intervals of reaction and analyzed by analytical method described above using UV–Visible spectrometer. The effect of pH on adsorption of As(III) was analyzed at different pH values (2–12) consistently using 1 mg/L initial concentration. For equilibrium study, 10 mg of His-MMt was added to 30 mL of As(III) solutions having different initial concentrations ranging from 10 to 90 mg.L\(^{-1}\). The sample solutions were stirred by giving 30 min contact time at 298 K to obtain adsorption equilibrium. In order
to investigate the effect of temperature on adsorption process, reaction was performed over the temperature range of 298–313 K. To analyze the effect of dosage amount, different weights of adsorbents ranging from 10 to 30 mg were mixed with mg.L⁻¹ of As(III) solution.

The percentage removal (%) and amount adsorbed per unit mass (mg g⁻¹) of As(III) was evaluated by following equation.

%Removal = \( \frac{C_i - C_e}{C_i} \times 100 \)  

(1)

\[ X = (C_i - C_e) \times V \]

where \( C_i \) and \( C_e \) are initial and equilibrium concentration of As(III) solution (mg.L⁻¹), respectively. \( V \) is volume of solution in L and \( X \) is adsorption capacity in mg/L.

### Statistical Evaluation of adsorption data and adsorption isotherm models

To verify the adsorption process statistically, a relation of Probability distribution function (PDF) was used in the form

\[ f(x) = \frac{df}{dx} \]

where the \( f(x) \) represents the Probability distribution function (PDF) and \( df \) indicates the cumulative distribution function CDF and the differential of (CDF) is equal to the PDF.

\[ \int_{-\infty}^{x} f(x)dx = F(x) \]

(4)

To verify the well-fitting of adsorption isotherm models, a statistical model known as absolute average relative deviation percentage (AARD) was used which can be described as

\[ \text{AARD} = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{q_i - q_e}{q_e} \right| \]

(5)

where \( N \) is no of data points, \( q_e \) and \( q_i \) are experimental and theoretical values of adsorption capacity (mg/g) respectively. Similarly, another statistical model known as Akaike’s information criterion (AIC_corrected) was used for verification of most suitable fitted adsorption isotherm which can be presented as

\[ \text{AIC}_{\text{corrected}} = \text{AIC} + \frac{2K(K + 1)}{N - K - 1} \]

(6)

where \( K \) is the number of parameters, while \( N \) is number of data points. AIC can be evaluated by error sum of squares by using following equations

\[ \text{AIC} = N \ln \left( \frac{\text{SSE}}{N} \right) + 2K \]

(7)

where SSE can be calculated by the relation

\[ \text{SSE} = \sum (q_e - q_t)^2 \]

(8)

### Characterization techniques

The Na-MMt modified by L-Histidine was characterized by using different characterization techniques. The modification of Na-montmorillonite was confirmed by Fourier Transform Infrared (FTIR) spectra of the sample recorded by SCHIMADZU 8202PC model in the wavenumber range 4000–400 cm⁻¹. Further the replacement of Na by L-Histidine was confirmed by XRD for XRD patterns by using Philips 1700 series X-ray diffractometer with Cu Kα radiation (\( \lambda = 0.1542 \) nm) operating at 40 kV voltage and 40 mA current. The thermal stability of both unmodified and modified adsorbent was checked Thermogravimetric analysis (TGA) and point of zero charge (PZC) was determined by well-known salt addition method reported in literature (Shah, Fahad et al. 2021). For this purpose, solutions of 0.1 M NaCl (40 mL) were prepared and their initial pH (pHᵢ) values were adjusted in the pH range of 2–12 using 0.01 M HCl or NaOH. In these adjusted pH solutions, 10 mg of adsorbent was poured and suspensions were stirred for 24 h. Then after stirring, final pH (pHᵢ) of solution was measured and a graph was plotted between pHᵢ and ΔpH and PZC was determined from the point of intersection where ΔpH = 0.

### Preparation of adsorbent

Montmorillonite was first converted into its sodium form by treating montmorillonite with 1 M NaCl. In 20 g of montmorillonite, 1 M NaCl was added and stirred for 24 h. After treating with NaCl the sample was washed for several times to remove excess ions. The sample was dialyzed by using dialysis membrane with deionized water until it becomes free from extra Na⁺ and Cl⁻ ions. The sample was then dried at 80 °C for 24 h. The Na-MMt was grinded with mortar and pestle and then passed through 250 μm sieve to collect fine Na-MMt particles. After that 20 g of Na-MMt was added in 1000 mL of deionized water and then 0.05 g of L-Histidine was added keeping pH of solution in the range of 4–5. The mixture was agitated at 300 rpm for 24 h to immobilize L-Histidine on the surface of Na-MMt solid support and then filtered. Then His-MMt was dried in oven for 24 h and grounded by passing through 200 mesh sieves and stored for performing adsorption experiments.
Results and discussions

Determination of point of charge (PZC)

PZC is a point where net surface charge of the adsorbent becomes to zero, and it can provide the possible mechanism for the interaction between adsorbent and adsorbate. The pH_pzc values of 6 and 9 were obtained for Na-MMt and His-MMt respectively as shown in Fig. 1.

FTIR results

The FTIR Results of Na-MMt, His-MMt and after adsorption of As (III) by His-MMt are shown in Fig. 2. The results indicated that Na-MMt and His-MMt showed broad O–H stretching vibration at 3620 and 3640 cm\(^{-1}\), respectively. The peak at 1635 cm\(^{-1}\) is due bending vibration of interlayer water or structural water in Na-MMt. The peaks at 1122 and 999 cm\(^{-1}\), were caused by inside and outside plane stretching vibration of Si–O bonds. In L-His-MMt, these corresponding peaks shifted to 1652, 1138 and 1018 cm\(^{-1}\). The bands observed at 3382 and 1424 cm\(^{-1}\) were assigned as N–H stretching vibration and imidazole ring stretching vibration of L-Histidine respectively. These results showed that L-Histidine has been successfully inserted into inter-layers of Na-MMt. When His-MMt adsorbed As (III), the corresponding peaks shifted to 3619, 1653 and 1020 cm\(^{-1}\) while 3382 cm\(^{-1}\) disappeared indicating that interaction of His-MMt with As (III) occurred via surface complexation reaction (Chu et al. 2020).

SEM analysis

The SEM results of Na-MMt and His-MMt are shown in Fig. 3. Lamellar structures of both Na-MMt and His-MMT were displayed. After adding of L-Histidine, the original lamellar structure of montmorillonite is not distorted, which confirmed that there was no exfoliation of the montmorillonite and the layered assembly of montmorillonite was protected in the whole process of modification. It also indicated that His-MMt has better dispersity and a more regular structure than Na-Montmorillonite.

TGA results

The TGA graph for thermal stability of Na-MMt and His-MMt is shown in Fig. 4. The results showed that His-MMt has a bigger weight loss as compared to Na-MMt. The curve of Na-MMt is composed of two regions. First region comes from 104 to 160 °C, where percentage loss is about 1.8% which may be due to the loss of physical or structural water and second region comes from 450 to 720 °C, where percentage loss is about 7.5% which may be due to the dehydroxylation of montmorillonite. For His-MMt curve, percentage weight loss is 2% in range of 90–125 °C, which may be due the evaporation of water and thermal degradation of L-Histidine. The second weight loss is 8.1% in the range of 450–712 °C which is due to break down of amino acid molecules (Chu et al. 2020). The comparative analysis of Na-MMt and His-MMt curves showed that the stability in material before and after modification was controlled by layered structure of montmorillonite. By incorporating L-Histidine into the layered structure of montmorillonite, the stability of montmorillonite was maintained.
XRD results

The results for XRD analysis are shown in Fig. 5. The d spacing value of Na-MMt was calculated as 2.26 nm at a diffraction peak $2\theta = 12.57^\circ$. The value of d. spacing was increased from 2.26 to 3.36 nm which showed that L-His-tidine was successfully inserted into the interlayer of Na-MMt structure. After adsorption of As(III) on His-MMt, new peaks appeared at $2\theta = 19.94^\circ$, 28.23°, 9.08° showing metal ions interaction with L-Histidine montmorillonite.

Effect of time

The results for the influence of contact time on adsorption process are shown in Fig. 6a which showed that percentage removal of As(III) onto His-MMt was increased with increasing contact time and maximum percentage removal (85.5%) of As (III) was achieved within 30 min of equilibrium time. Beyond 30 min, further no increase in removal efficiency was observed indicating the saturation of surface active site of adsorbent after 30 min. Therefore, 30 min contact time was optimized for further adsorption experiments.

The PDF model also statistically verified the kinetic curve and 30 min contact time for maximum uptake as shown in Fig. 6b. Once the plateau phase was achieved at 30 min, As(III) adsorption did not alter significantly with time and, hence, this PDF could be used for class statistical comparisons of As(III) adsorption rate and adsorption maxima.

To evaluate the kinetic data of As(III) removal by using L-Histidine Montmorillonite adsorbent, various kinetic models such as pseudo-first order and pseudo second order...
were used. The linearized form of pseudo first order kinetic model is given as:

\[
\ln \left( \frac{q_e - q_t}{q_e} \right) = \ln q_e - k_1 \ln t
\] (9)

where \( k_1 \) is the first order rate constant having unit \( \text{min}^{-1} \), \( q_e \) is adsorption capacity at equilibrium (mg/g), \( q_t \) is the adsorption capacity at time \( t \) (mg.g\(^{-1}\)). Similarly, linearized form of pseudo second order kinetic model can be written as:

\[
\frac{t}{q_e} = \frac{1}{K_2q_e^2} + \left( \frac{1}{q_e} \right) t
\] (10)

where \( q_t \) and \( q_e \) have the same meanings as described above and \( K_2 \) is the second order rate constant. The results of these plots are shown in Fig. 7a, b showing the higher value of regression coefficient \( R^2 = 0.999 \) for pseudo-second order model as compared to pseudo-first order model. This corresponds to well-fitting of pseudo second order kinetics model. Moreover, the Fig. 7c, d also show the well-fitting of intraparticle diffusion model as compared to film diffusion with higher value of regression coefficient \( R^2 = 0.995 \). All the kinetic parameters and regression coefficient values calculated from kinetic models are listed in Table 1.

Effect of pH

The adsorption of As (III) by His-MMt was strongly affected by pH of the solution. The results are shown in Fig. 8a which showed that adsorption efficiency of adsorbent was increased with increasing pH of solution and maximum adsorption was occurred at pH 6. As discussed earlier, the PZC of adsorbent was determined at pH 9, where net surface charge of adsorbent was zero, below pH 9 adsorbent surface was positively charged while above pH 9 was negatively charged. It can be observed from the figure that the percentage removal of As(III) was less at pH < 2 which can be explained by the fact that in highly acidic conditions, most abundant species of As(III) solution are neutral H\(_2\)AsO\(_3\) species and their adsorption ability is generally low. Because H\(^+\) ions and H\(_2\)O molecules are preferred by the surface of adsorbent for adsorption (Shah, Fahad et al. 2021). When the pH of As(III) solution was increased the OH\(^-\) ions combine with H\(^+\) ions of Arsenite species H\(_2\)AsO\(_3\) and resultant anionic species in As(III) solution appeared as H\(_2\)AsO\(_3\)\(^-\), HAsO\(_3\)\(^-\), and AsO\(_3\)\(^-\). Below pH 9, the positively charged surface of adsorbent adsors anionic species such as H\(_2\)AsO\(_3\)\(^-\), HAsO\(_3\)\(^-\), and AsO\(_3\)\(^-\). At pH greater than 9, the most dominant species of Ar(III) solution are AsO\(_3\)\(^-\) and, negatively charged surface of adsorbent repels anionic species AsO\(_3\)\(^-\). Therefore, the adsorption of As(III) was decreased at higher pH greater than PZC. The possible binding mechanism can be proposed as surface complexation where As(III) ions stabilize on adsorbent surface through electrostatic force of attraction and hydrogen bonding. The probability of As(III) uptake by the adsorbent also increases with increase of pH from pH 2 to 6, the maximum probability of As(III) uptake was found at pH 6 as shown in Fig. 8b. Thus PDF model provided a unique statistical approach for evaluation of adsorption data by providing a good fit for As(III) removal under the influence of different pH values of solution.

Effect of dosage of adsorbent

The dosage of adsorbent highly effected the removal of As(III) from aqueous solution as shown in Fig. 9a. The results demonstrated that removal efficiency of As(III) was
increased linearly with the increase of amount of adsorbent and maximum percentage removal of 93% achieved with optimum dose of 30 mg of adsorbent. From the results it can be observed that considerable increase in uptake of As(III) occurred when the amount of adsorbent was increased from 10 to 20 mg.

This may be due of availability of more active sites and surface area of adsorbent for mass transfer. However, beyond 30 mg of adsorbent, no further increase in removal efficiency was observed. This might be attributed to the aggregation or intersection of the absorbent particles and decrease the effective surface area of adsorbent when the amount of adsorbent was increased (Shah, Fahad et al. 2021). The probability of uptake of As(III) from adsorbent was also increases with increase of amount of adsorbent up to a certain range i.e. maximum when amount of adsorbent was 20 mg as shown in Fig. 9b

**Effect of temperature and thermodynamic investigation**

The effect of temperature on adsorption of As(III) by the adsorbent studied and results are shown in Fig. 10a. The
percentage removal of As(III) onto the adsorbent was increased with temperature because increasing temperature provide sufficient amount of kinetic energy to As(III) ions to undergo an interaction with active site at the surface of adsorbent. It can also be inferred from the results in figure that percent removal is higher in the range of temperature 298-308 K and there is a linear increase in As(III) adsorption. However, after 308 K, the rate of percentage removal was low and there is a gradual increase in adsorption was observed. After 318 K, the adsorption curve became almost parallel to the x-axis and ultimately reached at the stage of boundary adsorption due to saturation of adsorption active sites. Figure 10b presents the well fitness of PDF statistical model to the available experimental adsorption data. It can observe from the Figures, Fig. 10a, b that the shapes of PDF and experimental adsorption curve are statistically equivalent. This clearly indicates the robustness of PDF model for the evaluation of adsorption data. The thermodynamics parameters including Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) observed and the computed values for all thermodynamic parameters are presented in Table 1. The values of ΔH and ΔS were determined from the slope and intercept of Vant Holf plot while ΔG was calculated from Gibbs free energy. The relationship of ΔG, ΔH and ΔS can be provided by the following equation:

\[
\Delta G = \Delta H - T \Delta S
\]
where $K_c$ is the equilibrium constant. The values of $\Delta H$, $\Delta S$ and $\Delta G$ (Table 1) were obtained by using the following equation:

$$\ln K_c = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

$$\Delta G = \Delta H - T\Delta S$$

Table 2 shows that the values of $\Delta G$ at all temperatures are negative and hence showed the favorable and spontaneous nature of adsorption reaction, while the positive $\Delta H$ and $\Delta S$ values shows the endothermic nature of adsorption process and increase of overall randomness of the system, respectively. Parameters of different adsorption isotherm models are listed in Table 3.

**Effect of concentration**

The effect of initial metal ions concentration on the adsorption efficiency of As (III) onto His-MMt is investigated in detail and it is concluded that with the increase in concentration of metal ions, the adsorption capacity is also
increased (Fig. 11a). It can be predicted from figure that initially, the percentage removal of As (III) is increased by the adsorbent and after a certain limit, an equilibrium established and no further increase in the percentage removal of As (III) is observed. The reason is saturation of the available active sites of the adsorbent. The equilibrium study data is verified well through PDF as shown in Fig. 11b.

In order to understand the adsorption mechanism different adsorption isotherms models are applied on equilibrium study data such as Langmuir isotherm, Freundlich isotherm, Temkin isotherm and Dubinin-Radishkevich (D-R) isotherms as shown in Fig. 12a-d. It can be observed that Langmuir model is best applicable to the equilibrium data due to higher regression-coefficient ($R^2 = 0.9999$). The maximum percentage removal of As (III) ions is observed as 87% by the adsorbent when the concentration of As(III) solution was 200 ppm. The equation for Langmuir adsorption isotherm is given as:

$$\frac{C_e}{X} = \left(\frac{1}{q_m}\right)C_m + \frac{1}{K_Lq_m}$$  \hspace{1cm} (13)

Here, $C_e$ is concentration at equilibrium (mg.$\text{g}^{-1}$), $X$ is quantity of adsorbate adsorbed per unit mass of adsorbent (mg.$\text{g}^{-1}$), $q_m$ is maximum adsorption capability of adsorbent (mg/g) and $K_L$ is Langmuir constant for determination of maximum energy of adsorption. The equation for Freundlich adsorption isotherm is given as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$  \hspace{1cm} (14)

Here, $C_e$ is concentration at equilibrium, $q_e$ is amount of adsorbate per unit mass of adsorbent (mg.$\text{g}^{-1}$), $K_F$ is adsorption capacity and $1/n$ is heterogeneity factor showing adsorption intensity.

The equation for Temkin isotherm can be expressed in the form:

$$q_e = \frac{RT}{b_t} \ln A_t + \frac{RT}{b_t} C_e$$  \hspace{1cm} (15)

Here, $A_t$ (L.$\text{mg}^{-1}$) is Temkin isotherm constant while $b_t$ (K.$\text{mol}^{-1}$) constant related to heat of adsorption.

To understand whether the adsorption was physical or chemical, the mean free energy ($E$) from D-R isotherm was calculated, which can be expressed with the following equation:

$$\ln X = \ln Xm - \beta \varepsilon^2$$  \hspace{1cm} (16)

In Eq. (3), $\varepsilon$ is Polanyi adsorption potential and is equal to:

Table 3 Parameters of different adsorption isotherm models

| Adsorption Isotherms | Parameters       | Values  |
|----------------------|------------------|---------|
| Langmuir Isotherm    | $Q_m$ (mg/g$^{-1}$) | 87.71   |
|                      | $K_L$            | 0.0771  |
| Freundlich Isotherm  | $K_F$            | 9.506   |
|                      | $N$              | 0.6029  |
| Temkin Isotherm      | $B_T$ (J/mol$^{-1}$) | 123.3 @ |
|                      | $A_T$ (L/mg$^{-1}$) | 2.356   |
| DR-Model             | $Q$              | 50.28   |
|                      | $\beta$ (KJ/mol$^{-1}$) | 14       |

Fig. 11  a Effect of Concentration on adsorption process by His-MMt  b PDF of concentration study
The relationship of $\varepsilon^2$ to $\ln X$ is shown in the form of a plot following Dubinin-Radishkevich isotherm model in Fig. 12d. The value of free energy determines whether the process is physical or chemical adsorption which is related to the value of $\beta$ (mol$^2$.J$^{-2}$) as shown by the following relationship:

$$E = \frac{1}{(2\beta)^{1/2}}$$

(18)

The adsorption energy $E$ (kJ.mol$^{-1}$) calculated by D-R model is 14 kJ.mol$^{-1}$ which demonstrated the involvement of electrostatic force of attraction for the surface complexation reaction. between adsorbate ions and adsorbent (Behdani et al. 2013).

Statistical evaluation of adsorption isotherm by AIC corrected and AARD

The different adsorption isotherms were evaluated by Akaike information criterion AIC$_{corrected}$ and absolute average relative distribution (AARD) as shown in Fig. 13a, b. Based on overall results of AIC$_{corrected}$ and AARD the correlating ability of various isotherms found to be in ascending order as; Langmuir isotherm, DR model, Freundlich isotherm and Temkin isotherm respectively. Here the order of correlating ability for AIC$_{corrected}$ and AARD matches exactly.

The AIC$_{corrected}$ value for Langmuir adsorption isotherm was found as 3.19, while AARD value for Langmuir adsorption isotherm was found as 0.0368. It is cleared from the Fig. 13 that for Langmuir adsorption isotherm AIC$_{corrected}$ and AARD has least value, which demonstrated that this model is best fitted than other adsorption isotherm models.
applied in current equilibrium data (Rajahmundry et al. 2021).

The different materials used in literature for the removal of As(III) from water and the maximum adsorption capacity is shown in Table 4. The following comparison have shown that L-Histidine immobilized montmorillonite used in current investigation has high adsorption capacity as compared to other adsorbent materials.

Conclusions

The L-Histidine is successfully immobilized onto montmorillonite surface and this modified montmorillonite is explored in detail for its adsorption efficiency towards As(III). The maximum adsorption of 96% was obtained for As(III) following optimum experimental conditions that are pH 6.2, 20 mg L \(^{-1}\) initial concentration, 20 mg of adsorbent dosage, and for a contact time of 30 min at 318 K. Both Langmuir adsorption isotherm and pseudo-second order kinetic models were observed as the best fit to the adsorption data with high regression co-efficient values. A maximum As(III) adsorption capacity of His-MMt calculated through Langmuir isotherm is found to be 87.7 mg g \(^{-1}\) that is much higher compare to several others adsorbents reported in literature. The thermodynamic investigation confirmed the endothermic and spontaneous nature of adsorption process with increasing entropy at solid-solution interface. The probability distribution function (PDF) also validated the experimental adsorption data statistically and thus recommended to be used for the verification of data in similar adsorption studies. The lowest values of AIC\textsubscript{corrected} and AARD statistical models for Langmuir isotherm as compared to other isotherm applied to experimental equilibrium data represents that the adsorption phenomenon of His-MMt is best fit to the Langmuir isotherm. The results showed that L-Histidine immobilized montmorillonite was an excellent adsorbent material for As(III) adsorption. Moreover, the statistical models such as PDF, AIC\textsubscript{corrected} and AARD are very useful in verification of experimental data in adsorption studies.

Table 4  Comparison of L-Histidine immobilized montmorillonite with different clay based adsorbents for As(III) removal

| Sr. No | Adsorbents                                                                 | Maximum adsorption capacity \(q_m\) (mg g \(^{-1}\)) | References                  |
|--------|---------------------------------------------------------------------------|----------------------------------------------------|-----------------------------|
| 1      | Hydroxyapatite bentonite clay nanocrystalline cellulose                    | 51.01                                              | (Hokkanen et al. 2019)      |
| 2      | Sodium montmorillonite                                                     | 9.71                                               | (Zehhaf et al. 2015)        |
| 3      | Iron oxide coated sand                                                     | 0.14                                               | (Vaishya and Gupta 2003)    |
| 4      | Co-bentonite with MgO and poly (dimethyldiallylammonium)                  | 9.99                                               | (Hua 2018)                  |
| 5      | Al/Fe modified montmorillonite                                            | 3.854                                              | (Almasri et al. 2018)       |
| 6      | Iron coated sand                                                           | 0.0285                                             | (Gupta et al. 2005)         |
| 7      | L-Histidine immobilized Montmorillonite                                    | 87.7                                               | This study                  |

Fig. 13  a AIC\textsubscript{corrected}  b AARD for different isotherm models
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Declarations

Conflict of interest The authors declare no competing financial interest.

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