Ultrasound–acid modified *Merremia vitifolia* biomass for
the biosorption of herbicide 2,4-D from aqueous solution
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**ABSTRACT**

In this work, a biosorbent was prepared by the ultrasound–acid treatment of *Merremia vitifolia* plant and tested for the removal of 2,4-dichlorophenoxyacetic acid (2,4-D), a phenoxy herbicide. Optimal values of five batch biosorption parameters namely stirring speed, contact time, biosorbent dosage, initial pH and initial adsorbate concentration were experimentally obtained in sequential manner for an enhanced biosorption capacity. The kinetics of the biosorption of 2,4-D were best described by the pseudo first order kinetic model ($R^2 = 0.99$) and the biosorption equilibrium data were successfully fitted to the Langmuir adsorption isotherm ($R^2 = 0.99$) with a maximum biosorption capacity of 66.93 mg g$^{-1}$. The mechanism of biosorption was investigated using two intraparticle diffusion models (Weber and Boyd), Dubinin–Radushkevich isotherm model and electrostatic interactions. The presence of intraparticle and film diffusion limitations for the biosorption was confirmed along with the physical and chemical nature of the biosorption. The thermodynamic parameters of the biosorption were calculated using the equilibrium data obtained at four different temperatures. The entropy change for biosorption was found to be negative indicating the decreased randomness at the interface. Desorption studies were carried out using different solvents and the percentages of desorption were compared.

**Key words** | 2,4-dichlorophenoxyacetic acid, biosorption, herbicide, *Merremia vitifolia*, ultrasound–acid modification

**HIGHLIGHTS**

- A biosorbent from *Merremia vitifolia* biomass was prepared with ultrasound–acid treatment with carefully chosen experimental conditions.
- The modified biosorbent exhibited superior characteristics for the biosorption of 2,4-dichlorophenoxyacetic acid (2,4-D) mainly due to drastic increase of surface area.
- Batch adsorption studies were carried out with the modified biosorbent for 2,4-D removal from its aqueous solution and the optimal values of the batch adsorption parameters were obtained.
- The mechanism of the biosorption was explained with reasons for the increased biosorption capacity of the modified biosorbent.
- The study highlights the utilization of *Merremia vitifolia* biomass of no significant economic value for the adsorptive removal of 2,4-D from its aqueous solution.

**INTRODUCTION**

The use of agrochemicals, mainly pesticides, has resulted in enhanced protection and productivity of crops worldwide. The incessant use of pesticides is leading to serious contamination of natural eco-systems with the presence of pesticide residues emanating as runoff from applied crop sites and handling losses. More than 60% of the pesticides...
employed are herbicides (Silva et al. 2004) and they have become a major threat to the environment due to their toxicity. 2,4-D is a widely used herbicide compound for the control of broad-leaved weeds and an important constituent of many herbicide mixtures. It is employed for different crop varieties such as wheat, maize and rice as well as in lawns and aquacultures as a plant growth regulator (Lelifajri et al. 2018; Zhang et al. 2018). 2,4-D is a possible human carcinogen and mutagen (Ma et al. 2018), can damage the liver and heart, and attack the central nervous system. As the reports from many developing nations indicated the presence of 2,4-D in the surface and ground waters, it is essential to devise suitable techniques for the removal of this carcinogenic compound.

The maximum allowable contaminant level of 2,4-D in water for irrigation and drinking purposes are 100 and 70 ppb respectively (Amiri et al. 2018) while the solubility of 2,4-D in water is 900 mg L\(^{-1}\). The half-life of 2,4-D differs based on the availability of oxygen in the contaminated zone. Among the several separation techniques (membrane technology, advanced oxidation process, catalytic process, ion exchange process, biological treatment and adsorption technique) that can be employed for the separation of 2,4-D (Amiri et al. 2018), adsorption is highly efficient, cost-effective and easily implementable for larger throughputs. The adsorption technique has been widely used for the removal of various contaminants from natural resources. Activated carbons are widely used adsorbents in wastewater treatment due to their large surface area and porosity; however, their high costs limit their use. The development of biosorbents with desirable properties such as good adsorption capacity and low cost from natural resources is a topic of research now (Salman et al. 2011; Aswani & Kumar 2015). In the present work, biosorbents were prepared using Merremia vitifolia, a commonly found terrestrial weed, for the removal of 2,4-D from aqueous solution. Merremia vitifolia, commonly known as grape-leaf wood rose, is a perennial and climbing plant, and distributed in south and south-east Asia. Due to its aggressive growth, this plant can be seen as biomass of lower economic value. Hence, the plant biomass was used for the development of biosorbent for the removal of 2,4-D.

For the preparation of biosorbent with superior characteristics, several techniques (physical, chemical, biological and their combination) have been employed. In the current work, acid treatment of biomass under ultrasonication was considered. The acid treatment alone can enhance the presence of hydroxyl groups with increased surface area for the biosorbent. Also, the formation of pores on the surface can lead to enhanced biosorption capacity (Ingle et al. 2018).

In this work, the Merremia vitifolia plant biomass was treated with dilute sulphuric acid (6% v/v) in presence of ultrasonic waves (20A) and the modified biosorbent was used for the removal of 2,4-D from its aqueous solution. The kinetics, equilibrium and mechanism of biosorption are also reported. The thermodynamic parameters calculated from the equilibrium data obtained at four different temperatures indicated the exothermic nature of the biosorption. The regeneration of biosorbent was analysed using different desorbing solvents.

**MATERIALS AND METHODS**

**Materials**

The analytical grade 2,4-D (97% purity) and sulphuric acid (98%) were purchased from Sigma Aldrich (USA) and Merck (India) respectively. All aqueous solutions were prepared using Millipore water. A standard stock solution of 2,4-D of 500 mg L\(^{-1}\) was prepared by dissolving 500 mg of 2,4-D in one litre of Millipore water. Working solutions of 2,4-D (20–200 mg L\(^{-1}\)) were prepared by the respective dilutions of the stock solution.

**Preparation and modification of biosorbent**

The Merremia vitifolia plants were collected from an agriculture field located near to the National Institute of Technology Calicut, Kerala, India. The collected plants were thoroughly washed and cleaned, and dried for 1 day at 105 °C. The dried plant shoot biomass was cut into small pieces, powdered and sieved for biomass samples of 100–150 micron particle size. This biomass is termed as unmodified Merremia vitifolia biosorbent (UMMVB). The UMMVB and the ultrasound–acid treated biomass (UAMVB) were tested for the removal of 2,4-D from its aqueous solution. The parameters for the ultrasound–acid treatment were systematically estimated.

**Characterizations of biosorbents**

The surface morphologies of UMMVB and UAMVB were studied using a scanning electron microscopy (SEM) analyser (JEOL model JSM-6390 LV). The surface functional groups were identified using a Fourier transform infrared (FT-IR) spectrometer (Cary 630, Agilent Technologies, Malaysia) in the range of 4,000–400 cm\(^{-1}\). The specific
surface areas were estimated by a Brunauer–Emmett–Teller (BET) surface area analyser (Belsorp max, MicrotracBEL Corp., Japan). The amorphous/crystalline nature of the prepared biosorbents was analysed using X-ray diffraction (XRD) analysis (Miniflex 600, Rigaku, Japan).

**Biosorption of pesticide**

All initial batch biosorption studies were carried out in 100 mL volume capacity beakers. In a beaker, the biosorbent was added to 50 mL of 2,4-D solution of 100 mg L$^{-1}$ concentration at native pH (without any adjustment of pH). Using a magnetic stirrer, the solutions were stirred at 250 rpm. At defined intervals of time, the samples of the supernatant were collected and centrifuged at 4,000 rpm for 10 minutes, and the concentrations of 2,4-D in the samples were measured using a double beam UV-Vis spectrophotometer (Perkin Elmer) at a wavelength of 284 nm (Salman et al. 2011). The amount of biosorption at time $t$ ($q_t$) and at equilibrium ($q_e$) were calculated using Equations (1) and (2) respectively (Salman et al. 2011; Lelifajri et al. 2018):

$$q_t = \frac{(C_0 - C_t)V}{W}$$

$$q_e = \frac{(C_0 - C_e)V}{W}$$

where $C_0$, $C_t$ and $C_e$ (mg L$^{-1}$) represent the solution concentrations of 2,4-D at the start of experiment ($t = 0$), at time $t$ and equilibrium respectively; $W$ (mg) is the mass of dry biosorbent; $V$ (mL) is the volume of 2,4-D solution; $q_t$ and $q_e$ are the amounts of biosorbed 2,4-D at time $t$ and equilibrium respectively. The effect of stirring speed, contact time, dosage of biosorbent, solution pH and initial concentration of 2,4-D on the biosorption were studied. In each experiment, the 2,4-D percentage removal was calculated using Equation (3) (Sahin & Emik 2017):

$$R\% = \frac{(C_0 - C_t)}{C_0} \times 100$$

**Biosorption isotherm studies**

The isotherm models relate the concentration of adsorbate in the solution with the biosorbed amount at equilibrium. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D-R) isotherm models were employed to model the 2,4-D biosorption on UAMVB at equilibrium.

The nonlinear form of the Langmuir model is given as in Equation (4) (Zhang et al. 2018):

$$q_e = \frac{bq_mC_e}{1 + bC_e}$$

where $C_e$ is the concentration of pesticide in the solution (mg L$^{-1}$) at equilibrium, $b$ (L mg$^{-1}$) is the Langmuir equilibrium constant related to rate of adsorption, $q_e$ (mg g$^{-1}$) is the amount of pesticide biosorbed per unit mass of biosorbent at equilibrium and $q_m$ (mg g$^{-1}$) is the maximum biosorption capacity for monolayer formation.

The Freundlich model can be employed to depict the biosorption on heterogeneous surfaces and multilayer adsorption. The nonlinear form of the Freundlich isotherm is given as Equation (5):

$$q_e = K_f C_e^{1/n}$$

The Freundlich constants $K_f$ and $n$ define the relative adsorption capacity (mg g$^{-1}$) of biosorbents and the intensity of biosorbents for the biosorption respectively (Zhang et al. 2018).

The Temkin isotherm model considers the biosorbent and sorbate interactions and assumes linear decrease of the heat of biosorption with the increase of surface coverage. The nonlinear form of the Temkin model is given as Equation (6):

$$q_e = bT \ln (A_T C_e)$$

where $A_T$ is the Temkin isotherm constant (L mg$^{-1}$) and $b_T$ is the Temkin constant associated with a parameter called $b_T$ (kJ mol$^{-1}$), represented by the variation of adsorbent energy. It can be calculated from Equation (7) (Shikuku et al. 2018), where $R$ (8.314 J mol$^{-1}$ K$^{-1}$) is the universal gas constant, $T$ is the absolute temperature (K) [adsorbate$^+$]$^-$

$$b_T = \frac{RT}{B_T}$$

The D–R adsorption isotherm model is a commonly used and more general model compared to Langmuir and Freundlich isotherm models. It is widely used in solid–liquid adsorption systems (Zhou 2020). The nonlinear form of the D–R model is given below (Equation (8)):

$$q_e = Q_m \exp (Kc_e)$$

where $Q_m$ is the amount adsorbed at saturation. Here, $K$ represents the constant related to biosorption energy
(mol² kJ⁻²). The other constant $\varepsilon$ is known as polayani potential and it is calculated (Zhou 2020) as shown in Equation (9):

$$\varepsilon = RT \ln \left(1 + \frac{C^0}{C_e} \right)$$  \hfill (9)

where $C^0$ is taken as 1 mol dm⁻³ as the selected standard state and $C_e$ is the equilibrium concentration of adsorbate (mol dm⁻³).

### Batch biosorption kinetic studies

The kinetic studies of 2,4-D biosorption were carried out at the conditions obtained in the sequential optimization studies. The kinetic data of the biosorption was fitted for pseudo first order and pseudo second order kinetic equations. The nonlinear forms of pseudo first order and pseudo second order kinetic models are given in Equations (10) and (11) respectively (Lelifajri et al. 2018):

$$q_t = q_e (1 - e^{-k_1 t})$$ \hfill (10)

$$q_t = \frac{k_2 q^2 c t}{1 + k_2 q_c d}$$ \hfill (11)

where $q_t$ and $q_e$ are the amount of 2,4-D per gram of biosorbent corresponding to time $t$ and equilibrium respectively. $k_1$ (min⁻¹) is the pseudo first order rate constant and $k_2$ (g mg⁻¹ min⁻¹) is the pseudo second order rate constant of biosorption.

Prior to the biosorption of solute (adsorbate) on the surface of biosorbent, the adsorbate molecules must be transported onto the surface within the boundary layer surrounding the biosorbent particle. The identification of rate controlling steps for the biosorption is very important for the process design. Nevertheless, these details cannot be obtained using pseudo first and pseudo second order kinetic models.

A model called Weber's intraparticle diffusion model was used to explain the diffusion mechanisms involved in the biosorption. The model is expressed as Equation (12) (Calisto et al. 2019):

$$q_t = K_{di} t^{0.5} + C$$ \hfill (12)

where $K_{di}$ is the intraparticle diffusion rate constant (mg g⁻¹ min¹/²) and $C$ represents the thickness of the boundary layer. The values of these two parameters can be obtained from the plot of $q_t$ versus $t^{0.5}$. In many cases, the plot appears as multilinear representing the distinct transport phases of the adsorbate over the time.

The kinetic data were further examined using the Boyd model, in order to analyse the rate limiting step involved in the 2,4-D biosorption. The Boyd model can be expressed as Equation (13):

$$F(t) = \frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2BT)$$ \hfill (13)

where $F(t)$ is the fraction of biosorbed adsorbate at time $t$ and $BT$ is a function of $F(t)$. The value of $BT$ can be calculated using Equation (14) (Manzotti de Souza et al. 2019) and Equation (15):

$$BT = -0.4977 - \ln(1 - F(t)) \quad \text{for} \quad F(t) > 0.85$$ \hfill (14)

$$BT = \left(\sqrt{\pi} - \sqrt{\pi - \left(\frac{2F(t)}{3}\right)^2}\right)^2 \quad \text{for} \quad F(t) \leq 0.85$$ \hfill (15)

### RESULTS AND DISCUSSION

**Performance of biosorbents**

In the preliminary studies, we tested three different concentrations of H₂SO₄ (4, 6 and 10% v/v) for the acid treatment (duration: 24 hours each) of UMMVB. The biosorption studies were carried out using 50 mL of 100 mg L⁻¹ of 2,4-D solution at native pH and temperature with 0.1 g of the biosorbent. As shown in Figure S1 (Supplementary material), no noticeable increase in the biosorption capacity was observed for the treated biosorbent of 10% v/v concentration of H₂SO₄ in comparison to that of 6% v/v of H₂SO₄. Similarly, three different ultrasonication times were separately tested (15, 30 and 60 min) with no addition of acid. These results are also plotted in Figure S1. From these results, one can see that 6% v/v H₂SO₄ and 30 min ultrasonication time are quite acceptable for the ultrasound-acid treatment. The combined effect of H₂SO₄ concentration and ultrasonication time were studied as ultrasound-acid treatment with different ultrasonication times (15, 30 and 60 min) using 6% v/v H₂SO₄ (Figure S2). Nevertheless, higher acid concentrations and increased duration of ultrasonication could make the biosorption active sites unavailable due to pore structure damage. The maximum
removal percentage for biosorption of 2,4-D was obtained for the modified biosorbent of 30 min ultrasonication time in 6% v/v H₂SO₄ solution.

A comparison of UMMVB and UAMVB for the batch biosorption of 2,4-D was carried out and is shown in Figure S3. The UAMVB (6% v/v H₂SO₄, 30 min sonication) exhibited superior biosorptive removal characteristics in comparison to UMMVB. The pH of the solutions were not altered in these comparison experiments. At different pH values (pH: 2–10), the biosorption of 2,4-D by UMMVB was studied and the results are shown in Figure S4. The equilibrium percentage removal values at all tested pH values are less than that of UAMVB depicted in Figure S3. Since UAMVB exhibited superior biosorption characteristics compared to UMMVB, the effects of stirring speed, contact time, biosorbent dosage, initial solution pH, initial solution concentration and temperature on biosorption of 2,4-D were investigated for UAMVB (30 sonication in 6% v/v H₂SO₄).

Surface structural changes and the introduction of different active functional groups on the surface for the biosorbent are possible with ultrasound–acid modification. For a comparison, the UAMVB and UMMVB were characterized using FT-IR, SEM and BET surface area analyses to understand the effects of ultrasonication and the reasons for the increased biosorption capacity of the modified biosorbent. As mentioned earlier, detailed biosorption studies were conducted using UAMVB to obtain optimal conditions and equilibrium data. The equilibrium data was fitted to several isotherm models.

**FT-IR analysis**

The two biosorbents (UMMVB, UAMVB) were analysed using FT-IR in the range of 4,000–400 cm⁻¹. Many peaks that appeared in the case of UMMVB were shifted with varying intensity in the case of UAMVB as shown in Figure 1. The peak at 3,287 cm⁻¹ in the case of UMMVB was shifted to 3,220 cm⁻¹ for UAMVB. These peaks are attributed to the O-H and N-H stretching vibrations. The peak at 2,922 cm⁻¹ of UMMVB is attributed to –C–H stretching of the aliphatic group and it was seen at 3,049 cm⁻¹ with less intensity in the case of UAMVB. The intensity of the peak at 1,621 cm⁻¹ seen for UMMVB was reduced and shifted to 1,580 cm⁻¹ for UAMVB. These peaks indicate the bands of carbonyl groups (C=O) (Bahrami et al. 2018). The peaks at 1,380, 1,335 and 1,250 cm⁻¹ in the case of UMMVB represents the symmetrical COO⁻. The band peak in the case of UAMVB at 1,450 cm⁻¹ represents the O-H bending of the phenolic group (Nair et al. 2014). The new peaks appearing for UAMVB at 1,144, 1,075 and 1,005 cm⁻¹ correspond to C–O groups (Trivedi et al. 2016). The peaks present at 868 cm⁻¹ and 850 cm⁻¹ of the UAMVB represent the S(OH)₂ asymmetric stretch (Miller et al. 2005). Additionally, other new peaks at 665 cm⁻¹ and 582 cm⁻¹ in the case of UAMVB represent the out-of-plane bending of O–H group (Nair et al. 2014) and O=S=O bond (Miller et al. 2005) respectively. The FT-IR spectra of UAMVB after biosorption of 2,4-D is also shown in Figure 1. Peak shifts and disappearances of a few bands were seen in this case with respect to fresh UAMVB. The increased intensity of the peak at 1,580 cm⁻¹ indicates the C=O vibration of the adsorbed 2,4-D anion. Also, the peak shift from 665 cm⁻¹ to 693 cm⁻¹ indicates C–Cl stretching of 2,4-D (Trivedi et al. 2016).

**Surface morphology and specific surface area analysis**

The surface morphologies of the biosorbents were studied by SEM analysis and the images are shown in Figure 2. With the ultrasound–acid treatment, the morphological changes are quite evident. The surface of UAMVB (Figure 2(b)) is more porous than that of UMMVB (Figure 2(a)). This could be the primary reason for the increased biosorption capacity of UAMVB. In Figure 2(c), the SEM image of UAMVB post biosorption is shown. The surface morphology of UAMVB was changed but the porous nature was intact after the 2,4-D biosorption (Manna et al. 2016). The BET surface areas of UMMVB and UAMVB were 1.135 m² g⁻¹ and 172.8 m² g⁻¹ respectively. The enhanced surface area and availability of more active sites for
UAMVB were the main reasons for the increased biosorption of 2,4-D (Amiri et al. 2018).

X-ray diffraction analysis

The XRD analysis of UMMVB and UAMVB is shown in Figure S5. Data showed a broad peak at \(2\theta = 22\) for the two biosorbents, indicating a carbonaceous and amorphous nature of the biosorbents (Pandiarajan et al. 2018).

**BATCH BIOSORPTION OF 2,4-D USING UAMVB**

**Contact time and stirring speed**

The effect of contact time was studied with 0.1 g of biosorbent immersed in 50 mL of 100 mg L\(^{-1}\) 2,4-D solution with a stirring speed of 250 rpm. Figure S6 shows the percentage removal of 2,4-D for different contact times. The percentage removal was increased with the increase of contact time till 150 min, then almost remained constant, possibly due to the saturation of active sites (Manna et al. 2016). The influence of stirring speed was studied in the range of 100–300 rpm. The percentage removal of 2,4-D by UAMVB for the tested stirring speeds is shown in Figure S7. The increase in stirring speed resulted in the increased removal of 2,4-D up to 250 rpm. It can be due to the reduced film boundary layer surrounding the particles. Further increment in stirring speed beyond this optimum value could have reduced the time of contact between UAMVB particles and 2,4-D ions, thus lowering biosorption.

**Biosorbent dosage**

The effect of UAMVB dosage on 2,4-D removal was studied for three dosages (1, 2, 4 g L\(^{-1}\)). In the experiments, a fixed 2,4-D concentration of 100 mg L\(^{-1}\) was employed. The experiments were conducted at the room temperature without any alteration of solution pH. The biosorption capacity increased when the dosage was increased from 1 g L\(^{-1}\) to 2 g L\(^{-1}\). Further, no significant improvement in the removal percentage (Figure S8) was seen for the maximum dosage tested (4 g L\(^{-1}\)). If biosorbent is present above the optimum level, the possible agglomeration of biosorbent particles lowers the number of available surface active sites, thus resulting in an early saturation of surface for biosorption (Li et al. 2017). The optimum dosage of the biosorbent was fixed at 2 g L\(^{-1}\).

**Solution pH**

In order to study the effect of solution pH (range: 2–10) on uptake of 2,4-D, the biosorption studies were carried out using the optimized biosorbent dosage of UAMVB in 50 mL of solutions. The concentration of 2,4-D was set as 100 mg L\(^{-1}\). The pH of the solution was adjusted using 0.1 M HCl and 0.1 M NaOH at room temperature.

The influence of pH on 2,4-D biosorption is shown in Figure 3(a). The maximum removal of 2,4-D was seen at pH 6. Similar studies on the effect of pH on the biosorption of 2,4-D using magnetic Fe\(_3\)O\(_4\)@graphene nanocomposite was reported earlier (Liu et al. 2016). The effect of pH can be explained in terms of the point of zero charge (pHpZC) on the biosorbent surface. The point of zero charge of UAMVB surface was 6.5 as shown in Figure 3(b). The biosorption of 2,4-D is largely dependent on the surface charge and dissociation of 2,4-D in the aqueous media. The biosorbent surface becomes positively charged below its pHpZC and vice versa. As the pKa value of 2,4-D is 2.7 (Liu et al. 2016), the degree of dissociation of 2,4-D would be high when solution pH is above 2.7. The anionic form of 2,4-D gets biosorbed on the positively charged biosorbent.
surface when the solution pH is between 2.7 and 6.5. Since the maximum percentage removal was seen at pH value of 6, it was chosen as the optimum pH value. Further, the experiments were carried out with biosorbent dosage and pH values as 2 g L\(^{-1}\) and 6 respectively.

**Initial 2,4-D concentration**

The effect of initial solution concentrations of 2,4-D was studied in the range of 20–200 mg L\(^{-1}\) with the optimized values of pH and adsorbent dosage. The biosorption studies were carried out in 100 mL capacity beakers with 50 mL of 2,4-D solution (stirring speed: 250 rpm and contact time: 220 min at room temperature). The results are shown in Figure 4. The biosorption capacity of 2,4-D was increased with the increase of initial solution concentration and maximum removal (94%) was seen for 60 mg L\(^{-1}\). The removal percentage decreased for the increase of initial 2,4-D solution concentration beyond 60 mg L\(^{-1}\) and it is due to the unavailability of active sites for the fixed biosorbent dosage (Li et al. 2017).

**BATCH BIOSORPTION ISOTHERM STUDIES**

Figure 5 shows the fitted Langmuir, Freundlich and Temkin isotherms of 2,4-D biosorption on UAMVB at different temperatures. The Langmuir isotherm constants, \(q_m\) (mg g\(^{-1}\)) and \(b\) (L mg\(^{-1}\)), were calculated by the nonlinear fitting of \(q_e\) versus \(C_e\), and are shown in Table 1.

In order to understand whether the biosorption of 2,4-D by UAMVB is favourable or not, the dimensionless equilibrium parameter \(R_L\) was calculated using the Langmuir adsorption isotherm model’s constant \(b\) and the maximum initial concentration \((C_0)\) of the adsorbate (Pandiarajan et al. 2018). The expression for \(R_L\) is given in Equation (16).

\[
R_L = \frac{1}{1 + bC_0}
\]

The nature of the biosorption can be termed as favourable \((0 < R_L < 1)\) or unfavourable \((R_L > 1)\) based on this parameter value (Pandiarajan et al. 2018). In the current work, the calculated values of \(R_L\) at different temperatures (30, 35, 40 and 45 °C) are 0.007, 0.03, 0.04 and 0.09 respectively, suggesting favourable nature of 2,4-D biosorption on UAMVB. The maximum biosorption capacity and the \(R^2\) value were obtained as 66.93 mg g\(^{-1}\) and 0.99 respectively at 35 °C for the Langmuir isotherm model.
The constants \( K_f \) and \( n \) of the Freundlich isotherm model were obtained from the nonlinear fitting of \( q_e \) versus \( C_e \) and the values are shown in Table 1. Although the value of \( 1/n \) is less than 1.0 for all temperatures, indicating favourable nature of the biosorption (Pandiarajan et al. 2018), the average \( R^2 \) values of the Freundlich adsorption isotherm model fit at some temperatures were less than 0.95 confirming the non-suitability of the model.

The \( B_T \) and \( A_T \) values of the Temkin isotherm at different temperature were calculated (Table 1) from the nonlinear plot of \( C_e \) versus \( q_e \) (Figure 5). The variation in adsorbent energy \( (b_T) \) values at 30, 35, 40 and 45 °C were calculated as 1.0733, 0.1773, 0.322 and 0.3973 kJ mol\(^{-1}\) respectively. The average \( R^2 \) value is 0.96 for 40 °C suggesting unfavourable fit of the experimental data. The \( R^2 \) values are satisfactory at the lowest (30 °C) and highest

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**Table 1** Parameter values of different isotherm models for 2,4-D biosorption by UAMVB

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>30 °C</th>
<th>35 °C</th>
<th>40 °C</th>
<th>45 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( q_m ) (mg g(^{-1}))</td>
<td>18.94</td>
<td>66.93</td>
<td>38.56</td>
<td>29.39</td>
</tr>
<tr>
<td>( b ) (L mg(^{-1}))</td>
<td>0.70</td>
<td>0.18</td>
<td>0.11</td>
<td>0.054</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>Freundlich</td>
<td></td>
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</tr>
<tr>
<td>( K_f ) (L mg(^{-1}))</td>
<td>9.84</td>
<td>18.75</td>
<td>10.91</td>
<td>5.51</td>
</tr>
<tr>
<td>( n )</td>
<td>7.14</td>
<td>3.39</td>
<td>3.89</td>
<td>3.10</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.99</td>
<td>0.93</td>
<td>0.92</td>
<td>0.98</td>
</tr>
<tr>
<td>Temkin</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_T )</td>
<td>73.63</td>
<td>2.25</td>
<td>1.62</td>
<td>0.73</td>
</tr>
<tr>
<td>( B_T )</td>
<td>2.12</td>
<td>12.80</td>
<td>7.06</td>
<td>5.71</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.99</td>
<td>0.98</td>
<td>0.96</td>
<td>0.99</td>
</tr>
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</table>
(45 °C) temperatures tested for the Temkin isotherm, similar to the case with the Freundlich isotherm.

**BATCH BIOSORPTION KINETIC STUDIES ON 2,4-D REMOVAL**

The kinetics of 2,4-D biosorption were studied using pseudo first order, pseudo second order and intraparticle diffusion kinetic expressions (Equations (10)–(12)). The experiments were carried out at the optimized conditions of stirring speed (250 rpm), biosorbent dosage (2 g L⁻¹) and a solution pH of 6. The experimental values obtained for the different initial solution concentrations were fitted for the pseudo first and pseudo second order kinetic models by nonlinear fitting analysis. The parameter values of these models were calculated from the nonlinear fitting of $q_t$ versus $t$ (Figure 6(a) and 6(b)) and are tabulated in Table 2. Although the average $R^2$ values of both models are 0.99, the calculated $q_e$ values of the pseudo first order model were more close to the experimental values. Hence, the kinetics of biosorption are better represented by the pseudo first order model.

![Figure 6](https://example.com/figure6.png)

**Figure 6** | (a) Pseudo first order and (b) pseudo second order kinetic model plots of removal of 2,4-D by UAMVB at room temperature (35 °C).

**Table 2** | Kinetic parameter values of the biosorption of 2,4-D by UAMVB

<table>
<thead>
<tr>
<th>Initial conc. (mg L⁻¹)</th>
<th>$q_{e,exp}$ (mg g⁻¹)</th>
<th>$k_1$ (min⁻¹)</th>
<th>$q_{e,cal}$ (mg g⁻¹)</th>
<th>$R^2$</th>
<th>$k_2$ (g mg⁻¹ min⁻¹)</th>
<th>$q_{e,cal}$ (mg g⁻¹)</th>
<th>$R^2$</th>
<th>$K_{di}$ (mg g⁻¹ min⁻¹/₂)</th>
<th>$C$ (mg g⁻¹)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>9.38</td>
<td>0.031</td>
<td>9.15</td>
<td>0.97</td>
<td>0.0035</td>
<td>10.67</td>
<td>0.99</td>
<td>0.0035</td>
<td>0.197</td>
<td>0.86</td>
</tr>
<tr>
<td>40</td>
<td>18.68</td>
<td>0.024</td>
<td>18.72</td>
<td>0.99</td>
<td>0.0011</td>
<td>22.80</td>
<td>0.99</td>
<td>0.0042</td>
<td>0.969</td>
<td>0.90</td>
</tr>
<tr>
<td>60</td>
<td>28.28</td>
<td>0.019</td>
<td>28.6</td>
<td>0.99</td>
<td>0.0005</td>
<td>36.48</td>
<td>0.99</td>
<td>0.0030</td>
<td>0.755</td>
<td>0.73</td>
</tr>
<tr>
<td>80</td>
<td>37.47</td>
<td>0.013</td>
<td>40.559</td>
<td>0.99</td>
<td>0.0002</td>
<td>56.08</td>
<td>0.99</td>
<td>0.0027</td>
<td>0.713</td>
<td>0.75</td>
</tr>
<tr>
<td>100</td>
<td>44.31</td>
<td>0.021</td>
<td>45.36</td>
<td>0.99</td>
<td>0.0004</td>
<td>57.16</td>
<td>0.99</td>
<td>0.0038</td>
<td>0.936</td>
<td>0.87</td>
</tr>
<tr>
<td>140</td>
<td>56.27</td>
<td>0.024</td>
<td>56.56</td>
<td>0.99</td>
<td>0.0004</td>
<td>68.92</td>
<td>0.99</td>
<td>0.0040</td>
<td>0.955</td>
<td>0.88</td>
</tr>
<tr>
<td>180</td>
<td>51.38</td>
<td>0.043</td>
<td>59.08</td>
<td>0.98</td>
<td>0.0009</td>
<td>66.77</td>
<td>0.99</td>
<td>0.0032</td>
<td>0.355</td>
<td>0.85</td>
</tr>
<tr>
<td>200</td>
<td>61.98</td>
<td>0.054</td>
<td>59.83</td>
<td>0.99</td>
<td>0.0011</td>
<td>67.11</td>
<td>0.99</td>
<td>0.0033</td>
<td>0.197</td>
<td>0.86</td>
</tr>
</tbody>
</table>

$q_{e,exp}$ experimental value.

$q_{e,cal}$ calculated value.
MECHANISM OF 2,4-D BIOSORPTION

Intraparticle diffusion models

Figure 7(a) shows the Weber intraparticle diffusion model plot of 2,4-D biosorption, and three regions (stages I, II and III) are marked in the figure. The calculated values of $K_{di}$, $C$ and correlation coefficient ($R^2$) are given in Table 2. The initial stage (stage I) represents the instantaneous external surface biosorption. In the figure, the lines of stage II and III do not pass through the origin. In stage II, it can be implied that the diffusion of adsorbate onto the surface is not rapid as in the stage I. The stage III represents the near equilibrium stage of biosorption where the intraparticle diffusion is more significant. The non-passing of the linear lines of stage II and III through the origin represents the variations in mass transfer rate with time and the presence of rate limiting steps other than the intraparticle diffusion (Salman & Hameed 2010).

In order to study the rate limiting steps other than intraparticle diffusion, a plot of $BT$ versus $t$ is shown in Figure 7(b). As the linear fit lines of the data do not pass through the origin, film diffusion as a rate controlling factor is implied (Kalavathy et al. 2005). From these studies, it is confirmed that both intraparticle diffusion and film diffusion are significant during the biosorption process and they serve as the rate controlling factors for the 2,4-D biosorption on UAMVB.

D-R adsorption isotherm model

The D-R isotherm model is a favourable model to determine the nature of biosorption. The parameters of the model, i.e., $Q_m$ and $K$ were obtained (Table 3) from the nonlinear plot of $C_e$ and $q_e$ (Figure S9) at different temperature. The mean free energy $E$ (kJ mol$^{-1}$) of biosorption from the D-R model is calculated using Equation (17) (Manzotti de Souza et al. 2019):

$$E = \frac{1}{\sqrt{2K}}$$

A value of $E$ below 8 kJ mol$^{-1}$ indicates the nature of biosorption is physical, otherwise a chemical nature of biosorption. The values of $E$ at 30, 35, 40 and 45 ºC were found to be 8.04, 5.68, 5.85 and 5.15 kJ mol$^{-1}$ respectively, indicating the physical nature of the biosorption of 2,4-D on UAMVB.

Electrostatic interaction

The mechanism of 2,4-D biosorption can be explained on the basis of electrostatic interactions between UAMVB and 2,4-D ions. The biosorption of 2,4-D by UAMVB is quite dependent on the pH of the solution. The surface of UAMVB is neutral at pH 6.5 (pH$zpc$). If the solution pH is below 6.5, the surface of UAMVB becomes positively charged.

Table 3 | D-R isotherm model for biosorption of 2,4-D by UAMVB

<table>
<thead>
<tr>
<th>Model parameter</th>
<th>30 ºC</th>
<th>35 ºC</th>
<th>40 ºC</th>
<th>45 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_m$</td>
<td>0.00014</td>
<td>0.00081</td>
<td>0.00039</td>
<td>0.00034</td>
</tr>
<tr>
<td>$K$</td>
<td>0.00775</td>
<td>0.016</td>
<td>0.015</td>
<td>0.019</td>
</tr>
<tr>
<td>$E$</td>
<td>8.039</td>
<td>5.68</td>
<td>5.85</td>
<td>5.15</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Figure 7 | (a) Weber’s intraparticle diffusion model and (b) Boyd’s intraparticle diffusion model for the removal of 2,4-D by UAMVB at room temperature.
charged as given in Equation (18) and can attract negatively charged 2,4-D ion with the dissociation of 2,4-D

\[ \text{UAMVB} \xrightarrow{pH_{sec}} (\text{UAMVB})^+ \]  

(18)

The deprotonated form of 2,4-D at a pH of solution which is above the \( pK_a \) value of 2,4-D (\( \approx 2.7 \)), as shown in Equation (19), electrostatically binds the surface of UAMVB (Li et al. 2017).

\[ 2,4-D + OH^- \rightarrow 2,4-D^- \text{(deprotonated form)} + H_2O \]  

(19)

The FT-IR analysis of UAMVB indicates the presence of sulphur-containing functional groups (S(OH)\(_2\) asymmetric stretch and O-S=O bond). The presence of these functional groups also enhances the biosorption of 2,4-D ions on UAMVB, contributing to the chemical nature for the biosorption.

**BATCH BIOSORPTION THERMODYNAMIC STUDIES ON 2,4-D REMOVAL**

Biosorption thermodynamics elucidates the sorption mechanism in an isolated system where energy cannot be gained or lost, and the entropy change is the driving force. The changes in the three salient thermodynamic parameters (Gibbs free energy: \( \Delta G^0 \), kJ mol\(^{-1}\), enthalpy: \( \Delta H^0 \), kJ mol\(^{-1}\) and entropy: \( \Delta S^0 \), J mol\(^{-1}\) K\(^{-1}\)) were calculated to understand the spontaneity, heat and degree of randomness respectively for the 2,4-D biosorption by UAMVB. The values of the changes in the three thermodynamic parameters were calculated using the Equations (20)–(22) as given below (Lima et al. 2019):

\[
\ln K_{eq}^* = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]  

(20)

\[
K_{eq}^* = \frac{(1.000-b\times\text{molecular weight of adsorbate})\times[\text{adsorbate}]^+}{\gamma}
\]  

(21)

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0
\]  

(22)

where \( K_{eq}^* \) represents the thermodynamic equilibrium constant, is the molar concentration of the adsorbate (mol L\(^{-1}\)) and \( \gamma \) is the activity coefficient of the adsorbate (dimensionless). \( \Delta H^0 \) and \( \Delta S^0 \) were calculated from the slope and intercept of the plot between \( \ln K_{eq}^* \) and \( 1/T \) (Figure 8) and the calculated thermodynamic parameters are given in Table 4. The Gibbs free energy change for the 2,4-D on UAMVB is negative, which represents a spontaneous nature of biosorption (Sahin & Emik 2017). The increasing trend in the Gibbs free energy change values with the increase of temperature represents a favourable nature of biosorption. The negative value of \( \Delta H^0 \) (\( \approx -122.764 \) kJ mol\(^{-1}\)) indicates the exothermic nature of the biosorption (Calisto et al. 2019). Also, the negative value of \( \Delta S^0 \) points toward the decrement in the randomness at the biosorbent–adsorbate interface (Liu et al. 2016).

**DESORPTION STUDIES OF 2,4-D BIOSORPTION**

The regeneration studies of 2,4-D biosorption by UAMVB were carried out using different solvents; 0.1 g of UAMVB biosorbent with loaded 2,4-D was treated with 50 mL of the desorbing solution. The supernatants after desorption were analysed and desorption percentages were calculated (Figure S10). Among the different solvents used for...
desorption, 0.1 M NaOH solution yielded a maximum desorption of 30.76%. For other solvents, namely 0.1 M ethanol, 0.1 M H₂SO₄ and hot water, the percentage desorption values are 27.91, 4.62 and 8.8 respectively. Further studies are required to find the suitable solvent for the desorption of 2,4-D from UAMVB.

COMPARISON WITH PREVIOUS STUDIES

The current study utilizes ultrasound-acid modified Merremia vitifolia as biosorbent for the removal of 2,4-D from its aqueous solution. A comparison of the biosorption of 2,4-D by different adsorbents is listed in Table S1. Modified jute (Manna et al. 2016), organo-modified bentonite clay (Manzotti de Souza et al. 2019), magnetic graphene (Liu et al. 2016), bamboo biochars (Mandal et al. 2017), ultrasound–acid modified water hyacinth root biomass (Aswani & Kumar 2019) and nanomagnetic 3D polymer (3D/GO/Fe₃O₄) (Hajighasemkhan et al. 2020) were reported for the adsorptive removal of 2,4-D from aqueous solution. The comparison presented in Table S1 indicates the higher loading capacity of UAMVB for the biosorption of 2,4-D from its aqueous solution, showing its superior performance.

CONCLUSION

The present investigation reports UAMVB as a favourable biosorbent for the removal of 2,4-D from its aqueous solution. The ultrasound–acid modification of the native biosorbent (UMMVB) improved the biosorption capabilities for 2,4-D. For a better comparison, FT-IR spectroscopy, SEM and specific surface area analysis were carried out for both native and modified biosorbent. Notably, the BET surface area of UAMVB was almost 100 times that of UMMVB. The stirring speed, contact time, biosorbent dosage, solution pH and initial concentration of solute/adsorbate were optimized for the maximum biosorption capacity. The values of these parameters were found to be 250 rpm, 150 min, 2 g L⁻¹, pH 6 and 60 mg L⁻¹ respectively. The kinetics of biosorption were best described by the pseudo first order model and the equilibrium biosorption data followed the Langmuir isotherm model with a maximum biosorption capacity of 66.93 mg g⁻¹ at 35 °C.

To understand the mechanism of biosorption, the experimental data was modelled using two known diffusion models namely Weber and Boyd. The presence of rate limiting steps other than intraparticle diffusion was identified using Weber’s model. Also the Boyd model suggests that film diffusion is also a rate limiting factor for 2,4-D biosorption on UAMVB. The D-R isotherm model reveals the physical nature of biosorption. The dominance of electrostatic interactions for the biosorption of 2,4-D was established. The involvement of chemical interactions for the biosorption was also identified in the FT-IR analysis. The performance of UAMVB and other adsorbents for the removal of 2,4-D was compared and superior biosorption characteristics of UAMVB were noted. The biosorption was found to be spontaneous, favourable and exothermic in nature as per the thermodynamic analysis. Desorption studies were carried out using different desorbing solvents and a maximum desorption (30.76%) was obtained using 0.1 M NaOH as desorbing solvent. The current study effectively utilizes Merremia vitifolia plant weed for the preparation of a modified biosorbent (UAMVB) for the removal of 2,4-D from its aqueous solution.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


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