Mathematical modelling of water sorption isotherms and thermodynamic properties of wastewater sewage sludge

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Abstract

This study was aimed at determining wastewater sewage sludge moisture sorption characteristics using a static gravimetric method at 303 K, 313 K and 323 K. Eleven mathematical models were adopted to simulate the experimental data, and the optimal model was analysed. The indexes included the net isosteric heat of adsorption ($q_{st}$), differential entropy ($\Delta S$), spreading pressure ($\pi$), net integral enthalpy ($q_{in}$) and net integral entropy ($\Delta S_{in}$) to evaluate the thermodynamic properties of the sludge. The isotherm curves exhibited type II behaviour according to the Brunauer–Emmett–Teller classification. The sorption isotherm fitting showed that the Guggenheim–Anderson–de Boer model was able to reproduce the equilibrium moisture content evolution with water activity for a moisture range varying from 6% to 89% ($0.991 < R^2 < 0.999$). The net isosteric heat and differential entropy were evaluated through direct use of moisture isotherms via the Clausius–Clapeyron equation and used to investigate the enthalpy–entropy compensation theory. The net isosteric heat and differential entropy obviously decreased as the equilibrium moisture content increased, which satisfied the compensation theory. The spreading pressure of the sludge sorption process decreased as the temperature increased at a given water activity and increased as the water activity increased at a given temperature. When the spreading pressure was at a fixed level, the net integral enthalpy decreased as the equilibrium moisture content increased, whereas the net integral entropy decreased as the equilibrium moisture content increased to a minimum value of $-93.17$, $-98.34$ and $-93.28$ J/(mol.K) at 303 K, 313 K and 323 K, respectively, and then tended to increase.

Keywords: wastewater sewage sludge; water sorption isotherms; equilibrium moisture content; mathematical models; microscopic analysis

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1. INTRODUCTION

Wastewater sewage sludge (or municipal sewage sludge) is a semi-solid material formed in the process of sewage treatment. It contains water and refractory organics, heavy metals and salts, pathogenic bacteria and parasite eggs [1]. Wastewater sewage sludge is harmful to the environment and human health [2]. If sludge is not properly treated and disposed of, it may cause secondary pollution, and harmful components may eventually enter the food chain [3]. With the development of the global economy, acceleration of urbanisation, increase in urban population and continuous improvement of the sewage treatment rate, sludge production is increasing all over the world. From 2007 to 2013, China’s total sludge output increased yearly, with an average annual growth rate of approximately 13%. In 2013, China’s total dry sludge output was 6.25 million tons, and it has been estimated that this annual output will exceed 60 million tons within 2020–2025 [2]. Canada and the United States produce approximately 660 000 and 6.5 million tons, respectively, of dry sludge annually [4]. Moreover, researchers predict that by 2020, the annual dry sludge production in Europe will exceed 13 million tons [5].
Therefore, it is imperative to properly solve the sludge disposal problems of wastewater sewage treatment plants and to achieve the reduction, stabilisation, harm negation and resource utilisation of sludge. Various technologies such as landfilling, composting, agricultural utilisation and incineration can be used for sludge disposal or recovery [6]. The dominant routes for sewage sludge management currently present in the EU are landfills, soil application and incineration, and the amount accounts for almost 90% of the total sludge production [7]. In the United States and China, agricultural utilisation of sewage sludge is the primary route, but the application is limited by current laws and regulations requiring a high standard of sludge quality [8]. In Japan, the main method for sewage sludge management, used for the treatment of almost 48% of generated sewage sludge, is construction material manufacturing. The dry mass of sewage sludge contains organic carbon, which can be used for energy recovery via anaerobic digestion [9], co-incineration with coal [10] and biomass gasification [11].

The water content of the primary sludge resulting from preliminary treatment [12] and the secondary sludge resulting from biological processes in wastewater treatment plants can be as high as 98% [13]. Therefore, the water in sewage sludge is considered to be a worthless component, leading to an increase of difficulty in recovery or disposal [14]. The water fractions in sewage sludge can be classified as free, vicinal and bound water [15]. Mechanical dewatering in a wastewater treatment plant can dislodge free water, but difficulties occur in removing vicinal water and bound water from a sludge suspension's polymeric matrix [14]. Vicinal water adheres to the solid surface and can be eliminated through heating, whereas the removal of bound water requires changing the structure or composition of the sewage sludge, which can be achieved by dehydration. It is evident that for all proposed options of sewage sludge treatment, drying constitutes an important step. Many studies in the literature have analysed the sewage sludge drying process. The drying process and kinetics can be affected by any of the following factors: sludge thickness [16], drying temperature [17], air velocity [14], salt concentration [18], sludge water content, crack formation [19] and additives for improving the sludge’s combustion characteristics [20].

The hygroscopic character of sludge is not fully understood, possibly limiting progress in the development and optimisation of sewage sludge treatment technologies. Future research is needed to determine the hygroscopic character of sludge based on a fundamental understanding of sludge's sorption isotherms, which describe the relationship between the equilibrium moisture content and relative humidity of the environment surrounding the product for a given temperature [21]. It is the characteristic of the water sorption mechanisms and interactions between the solid skeleton and water molecules that takes place on a microscopic scale. Sorption isotherms have various practical and technical significances. They can offer information on the stability of materials and distribution and intensity of water bonds [22]. They are also important in the modelling of the drying process, design and optimisation of drying equipment and determination of wastewater sewage sludge.

Many water sorption isotherms of hygroscopic porous materials with a focus on agro-food products are available in the literature. Several theoretical, semi-theoretical and empirical models have been proposed and used by scholars and researchers to fit the equilibrium moisture content data reviewed as part of these models and report multiple common equations for fitting the sorption isotherms of different agro-food materials [23–26]. The moisture adsorption equilibrium of sludge has been studied at different temperatures and relative humidity values [22, 27, 28]. Bellur et al. [27] have found that the VCSM model is the most versatile model to accurately describe the water sorption in the ranges of 10%–84% relative humidity and 303 K–333 K. Remington et al. [28] have conducted a series of experiments on the sorption of fresh faeces at different water activities and presented the use of the GAB model for predicting water activity and calculating the sorption heat for drying. Bougayr et al. [22] have investigated the sorption isotherms of the sewage sludge generated at the wastewater treatment plant of Marrakesh city in Morocco at 303 K–323 K and stated that the Peleg model provides the best fit for describing the desorption and adsorption isotherm curves. All sorption isotherms from different studies have the same signate curves in different variation ranges of the equilibrium moisture content [22, 27, 28].

However, direct transfer of the moisture distribution characteristics from agro-food materials to wastewater sewage sludge is not possible because of considerable differences in the porous media characteristics [22]. Furthermore, based on a literature search on sorption isotherms, the thermodynamic properties of sewage sludge are limited to a description of differential changes, e.g. the net isosteric heat of adsorption and differential entropy, and lack analyses of the phenomenon. Comprehension of integral enthalpy and integral entropy is conducive to controlling and predicting the change of water and material binding energy during sewage sludge storage and to guiding practices in sewage sludge treatment. Therefore, the purpose of our study is (1) to establish the data of sludge equilibrium moisture content and water activity, (2) to evaluate the best isotherm equation of water adsorption, (3) to fit the experimental adsorption data, (4) to determine the thermodynamic properties (adsorption isotherm, differential entropy, net integral enthalpy and net integral entropy) and (5) to analyse the change trend phenomenon and the internal relationship of the parameters.

2. MATERIALS AND METHODS

2.1. Origin of sludge samples
The sewage sludge studied in this paper was from a sewage treatment plant, which was installed in Zhejiang Province, China PR. This sewage treatment plant’s phase II project has been in operation since 2011, with a service area of 1860 km². It is designed to treat a daily flow of 600 000 tons of sewage per day, which produces approximately 4.5 million tons per day of dewatered sludge. The samples were collected at different levels of the mechanical
conducted at 30°C in an incubator. The adsorption and desorption experiments were carried out with sludge samples. The jars were kept at a constant temperature in a refrigerator for further examination in the refrigeration and cryogenics laboratory of the University of Shanghai for Science and Technology. The initial moisture content of the experimental sample is 85 ± 1%.

### 2.2. Experimental procedure

There are several experimental methods for the determination of adsorption isotherms. In this work, we chose to use the static method of a saturated salt solution. We used KOH, MgCl₂, K₂CO₃, NaNO₃, KCl, BaCl₂, NaBr, NaCl and LiCl in preparing the solutions. A certain mass of dry sludge samples was weighed in containers with supersaturated solutions such as KOH, MgCl₂, K₂CO₃, NaNO₃, KCl, BaCl₂, NaBr, NaCl and LiCl. The water activity values of the saturated salt solutions at different experimental temperatures were taken from previous research and are given in Table 1.

The apparatus consisted of a series of nine 1000-ml glass jars, each of which contained 300 ml of saturated salt solution. Each jar had a sample holder, atop that was an open vial containing sludge samples. The jars were kept at a constant temperature in an incubator. The adsorption and desorption experiments were conducted at 30°C, 40°C and 50°C by adjusting the incubator’s temperature. Fresh samples were directly used in the sludge desorption experiments. For the adsorption experiment, the sample was dried in an oven at 105°C. The monitoring of the mass exchange that occurred between the sample and the jar’s atmosphere was conducted using an electronic scale with a digital display and a precision of 0.001 g. Each sample was weighed regularly every day until reaching a constant mass (the difference between two weights was no more than 0.001 g). Then, the dry mass of the sludge samples was determined after they were dried for 24 h in an oven at 105°C. The equilibrium moisture content (Mₑ) was determined using Eq. (1).

\[
Mₑ = \frac{Mₘ - M₀}{M₀} \times 100\%
\]

where \(Mₘ\) is product wet mass (kg), \(M₀\) is dry mass (kg).

### 2.3. Mathematical treatment

Owing to the complexity of the heat and mass transfer process of sludge, the experimental data of the isotherms were analysed using 11 mathematical equation models chosen from among the most used equations in the literature. The expressions and parameters of the models are summarised in Table 2. The parameters of each model were determined by minimising the difference between the calculated value and the experimental value. The MATLAB software was used for the nonlinear regression analysis and mathematical processing. The choice of the most suitable model for the adjustment of the isotherms of the sludge samples was based on the correlation coefficient \(R²\) and sum squared error (SSE) [14]. The adequate model had to present the smallest SSE and the highest coefficient of correlation \(R²\) [23]. These parameters were defined as follows:

\[
R² = \frac{\sum_{i=1}^{N} (M_{\text{calc},i} - M_{\text{exp},i})^2}{\sum_{i=1}^{N} (M_{\text{calc},i} - M_{\text{exp},i})^2} \quad (2)
\]

\[
\bar{M}_{\text{exp},i} = \frac{1}{N} \sum_{i=1}^{N} M_{\text{exp},i} \quad (3)
\]

\[
\text{SSE} = \frac{1}{N} \sum_{i=1}^{N} (M_{\text{exp},i} - M_{\text{calc},i})^2 \quad (4)
\]

where \(M_{\text{calc},i}\) is the predicted equilibrium moisture (kg/kg), \(M_{\text{exp},i}\) is the experimental equilibrium moisture (kg/kg), \(\bar{M}_{\text{exp}}\) is the average value of experimental equilibrium moisture (kg/kg) and \(N\) is the data values number. Eleven models were selected to fit the experimental data, as shown in Table 2.

The three parameters of the GAB model \((M_m, C \text{ and } K)\) were all functions of temperature, where \(M_m\) is the monolayer moisture content on the internal surface and \(C \text{ and } K\) are related to the sorption heat of the monolayer and multilayer, respectively. The

| Salt     | 303 K | 313 K | 323 K |
|----------|-------|-------|-------|
| KOH      | 0.0740| 0.0630| 0.0570|
| LiCl     | 0.1100| 0.1100| 0.1100|
| MgCl₂    | 0.3200| 0.3100| 0.300  |
| K₂CO₃    | 0.4300| 0.4300| 0.4200|
| NaBr     | 0.5600| 0.5300| 0.5100|
| NaNO₃    | 0.7300| 0.7100| 0.5800|
| NaCl     | 0.7500| 0.7500| 0.7100|
| KCl      | 0.8400| 0.8200| 0.7700|
| BaCl₂    | 0.9000| 0.8900| 0.8800|

| Models               | Mathematical expression |
|----------------------|-------------------------|
| Halsey [29]          | \(Mₑ = \left( -\frac{\ln(\text{water activity})}{T} \right)^{\frac{1}{b}}\) |
| Henderson [30]       | \(Mₑ = \left[ \ln \left( 1 - a_w \right) \right]^{\frac{1}{b}}\) |
| Oswin [31]           | \(Mₑ = K \left( \frac{a_w}{1-a_w} \right)^n\) |
| Smith [32]           | \(Mₑ = a + b \ln \left( 1 - a_w \right)\) |
| Lespam [23]          | \(Mₑ = k_1 e^{\frac{a_w}{k_2}} + b\) |
| Modified Halsey [22] | \(a_w = e^{-\left[ -a \left( \frac{1}{n} \right) \right] Mₑ} \) |
| Modified Henderson [33]| \(a_w = 1 - e^{-\left[ -\left( \frac{1}{n} \right) \right] Mₑ} \) |
| Modified Oswin [22]  | \(Mₑ = \left( \frac{k_1}{1-n\alpha_{\text{exp}}} + \frac{k_2}{\alpha_{\text{exp}} Mₑ \cdot C \cdot K} \right) Mₑ \) |
| GAB [34]             | \(Mₑ = k_1 e^{\frac{a_w}{k_2}} + k_3 a_w \) |
| Peleg [35]           | \(Mₑ = \left( 1 - K_{\alpha_{\text{exp}}} \right) \left[ 1 - K_{\alpha_{\text{exp}}} \right] \) |
influence of temperature on the parameters of the GAB model could be expressed by the Arrhenius equation [36, 37] as follows.

\[ M_m = M_{m0}e^{\frac{\Delta H}{RT}} \]  
(5)

\[ C = C_0e^{\frac{H_m-H_N}{RT}} \]  
(6)

\[ K = K_0e^{\frac{H_m-H_N}{RT}} \]  
(7)

where \( H_L \) is heat of water vapour condensation (43.30 KJ/mol), \( \Delta H \) is aronius energy level factor (KJ/mol), \( H_m \) and \( H_N \) are the sorption heat of the monolayer absorbed water and multilayer absorbed water, respectively (KJ/mol), \( R \) is universal gas constant (8.314 KJ/(mol.K)), \( T \) is temperature (K), \( M_{m0} \), \( C_0 \) and \( K_0 \) are entropic accommodation constants.

2.4. Thermodynamic properties

2.4.1. Net isosteric heat of adsorption and differential entropy

The drying operation concerned the heat required to remove water from the material, so the net adsorption heat was the basic parameter for designing the drying equipment. The net isosteric heat of adsorption is the amount of energy of water evaporation in materials exceeds the latent heat of pure water vapourisation under constant temperature and water activity [38]. It was calculated from the data obtained from the best fitting model using the Clausius–Clapeyron equation [39, 40].

\[ \left( \frac{d\ln a_w}{dT} \right)_{M_e} = - \frac{\eta_{st}}{R} \]  
(8)

where \( \eta_{st} \) is net isosteric heat of adsorption (KJ/mol), \( a_w \) is the water activity (dimensionless) and \( M_e \) is the moisture content (kg/kg).

Differential entropy refers to the attraction or repulsion of water molecules and material components, which can be used for energy analysis. It is associated with the number of water adsorption sites available at a specific energy level and can be calculated through the Gibbs–Helmholtz equation [41].

\[ \Delta S = \frac{\eta_{st} - \Delta G}{T} \]  
(9)

where free Gibbs energy is defined as

\[ \Delta G = -RT \ln \left( a_w \right) . \]  
(10)

The final formula, Eq. (11), was given by substituting Eq. (10) into Eq. (9) and rearranging. The differential entropy for a given equilibrium moisture content was calculated from the intercept of the linearised experimental curve of \( \ln a_w \) versus \( 1/T \) [42].

\[ - \ln a_w = - \frac{\eta_{st}}{RT} - \frac{\Delta S}{R} \]  
(11)

2.4.2. Enthalpy entropy compensation theory

Enthalpy and entropy compensation suggests that there is a linear relationship between enthalpy and entropy for determined moisture content [43]. The theory has been used to evaluate physical and chemical phenomena in desorption processes under varying conditions. The linear relation is as follows:

\[ q_{st} = T_\beta \Delta S + \Delta G \]  
(12)

\( T_\beta \) is the isokinetic temperature, which represents the temperature at which all reactions in the desorption series proceed at the same rate [44, 45]; \( \Delta G_\beta \) is the free energy at isokinetic temperature (\( T_\beta \)). The sign \( \Delta G_\beta \) can indicate whether water desorption is a spontaneous (negative) or non-spontaneous process (positive).

To corroborate the compensation theory, the isokinetic temperature (\( T_\beta \)) was compared with the harmonic mean temperature (\( T_{hm} \)), which was given as follows [46]:

\[ T_{hm} = \frac{N}{\sum_{i=1}^{N} \frac{1}{T_i}} \]  
(13)

where \( N \) is the number of isotherms used. The compensation theory was established if \( T_\beta \) and \( T_{hm} \) were significantly different. If \( T_\beta > T_{hm} \), the adsorption process was controlled by heat absorption (exothermic) and driven by enthalpy. If \( T_\beta < T_{hm} \), the adsorption process was controlled by the order of molecular motion and driven by entropy.

2.4.3. Spreading pressure

Spreading pressure is the force applied vertically on each unit length of the edge to keep the surface from spreading. It represents the excess free energy on the surface and reflects the driving force of water diffusion in porous media [47]. It can be obtained using an analytical procedure that reveals the relationship between moisture content and water activity [48].

\[ \pi = \frac{KT}{A_m} \int_0^{a_w} \frac{\theta}{a_w} da_w \]  
(14)

\[ \theta = \frac{M_e}{M_m} \]  
(15)

where \( M_m \) is the monomolecular layer moisture content that can be obtained by applying the GAB model equation to the experimental equilibrium moisture data. Thus, upon substituting Eq. (15) and the formula of the GAB model into Eq. (14) and rearranging, the integral incorporated in Eq. (16) could be tackled analytically, resulting in the mathematical description for the spreading pressure [49].

\[ \pi = \frac{K_BT}{A_m} \ln \left( \frac{1 + KCa_{aw} - Ka_{aw}}{1 - Ka_{aw}} \right) \]  
(16)
where \( k \) is constant related to total heat of sorption of multilayer, and \( C \) is the GAB constant related to monolayer properties.

### 2.4.4. Net integral enthalpy and net integral entropy

Net integral enthalpy represents the total available energy, which reflects the bonding strength of water molecules to a solid structure and has an effect on a drying process' energy balance [50]. The net integral enthalpy \( (q_{in}) \) was calculated here using a technique similar to that used for net adsorption heat but at a constant spreading pressure instead of a constant moisture content using Eq. (17), derived from the first law of thermodynamics [51].

\[
\left( \frac{d \ln a_w}{d \frac{1}{T}} \right)_{\pi} = - \frac{q_{in}}{R}
\]

Net integral entropy describes the disorder and randomness of water molecule movement and quantifies the fluidity of an adsorbed water molecule. This parameter is calculated as follows:

\[
\Delta S_{in} = - \frac{q_{in}}{T} - R \ln (a_W)^{*}
\]

where \( (a_W)^{*} \) is the geometric mean water activity obtained at a constant spreading pressure at different temperatures.

### 3. RESULTS AND DISCUSSION

#### 3.1. Adsorption and desorption isotherm

The experimental results of the equilibrium moisture content \( (M_e) \) as a function of water activity for adsorption and desorption are presented in Figure 1 for 303 K, 313 K and 323 K. The results illustrate the influence of temperature on the equilibrium moisture content, demonstrating that the content increases as the water activity increases at a constant temperature but decreases as the temperature increases at a given water activity. The reason for the phenomenon is that the water molecules are in a state of excitation at a high temperature and are easily separated from the original adsorption sites due to the decrease in the attraction forces of the water molecules between them [22]. Therefore, wastewater sewage sludge is less hygroscopic at higher temperatures. Similar experimental results have been reported by other researchers for different products [23] [38] [49, 52], specifically by Bougây on sewage sludge from Marrakesh.

It can clearly be seen from Figure 1 that the shapes of all sludge adsorption isotherms obtained in the experiment were anti-S type, belonging to type II in the IUPAC classification of adsorption isotherms [52]. Generally, the hygroscopic isotherms of biomass are classified as type II. The biopolymer grid structure in the large pores of the sludge has a strong binding force with water and can adsorb multiple layers of water. The adsorption form of the combined water and solids of the small pores is similar to a Langmuir-type adsorption curve.

#### 3.2. Mathematical modelling

Eleven mathematical models were tested to fit the experimental sludge data. Table 3 shows the values of the statistical parameters of the models, the \( R^2 \) and the SSE. The statistical parameters of the models showed that the GAB model was the most appropriate to describe the desorption and adsorption isotherms of the sludge. It had the highest \( R^2 \) (0.9989) and the lowest SSE (9.946 \times 10^{-5}). The isotherms smoothed by the GAB model for the three temperatures are presented in Figure 2. The GAB model was the most suitable to describe the sludge experiment in the entire water activity and temperature range of the experiment as long as it allowed for the physical explanation of the adsorption phenomenon [49, 53]. It could be used to predict the sludge isotherm and analyse the thermodynamic properties. It was also found to be a suitable model for different products such as foodstuff [38, 39] and wood [54].
However, the GAB model did not consider the effect of temperature on the adsorption isotherm but was only valid for isotherms at a fixed temperature. Thus, there was no clear relationship between the parameters (\(M_n\), C and K) and temperature through the observation of the fitting GAB model. As K constants are associated with the chemical potential difference in the pure liquid adsorbed and in the upper layers, examination of the fitting results in Table 3 showed that the K constants were lower than unity.
Figure 2. Isotherms of desorption and adsorption of sludge smoothed by the GAB model for the three temperatures: (a) adsorption at 30°C, (b) desorption at 30°C, (c) adsorption at 40°C, (d) desorption at 40°C, (e) adsorption at 50°C and (f) desorption at 50°C.

and that this was a definitive characteristic of the GAB model. The monolayer moisture content \( M_{\text{m}} \) indicates the minimum moisture content covering the hydrophilic parts on a material surface [50]; it is the best moisture content for storage and preservation and is related to many aspects of physical and chemical drying product deterioration [49]. It is also higher for adsorption than desorption [50]. The Guggenhiem constant \( C \) is considered an indicator of the difference of the chemical potential in the upper layers and the monolayer and is higher for desorption (Table 2). Here, the wastewater sewage sludge had high \( C \) values, demonstrating that the water molecules were strongly bound to the primary sorption sites, forming a strong monolayer [23].
Table 4. Characteristic parameters of GAB model.

| Characteristic parameters | Adsorption | Desorption |
|--------------------------|------------|------------|
| \( M_{m0} \)             | 0.3000     | 0.1729     |
| \( C_0 \)                | \( 1.0479 \times 10^{-9} \) | \( 6.0253 \times 10^{-9} \) |
| \( K_0 \)                | 1.3295     | 1.4221     |
| \( \Delta H(\text{kJ/mol}) \) | 7.4472     | 8.7573     |
| \( H_M-H_N(\text{kJ/mol}) \) | 63.3224    | 64.9161    |
| \( H_L-H_N(\text{kJ/mol}) \) | \(-1.3112\) | \(-1.4827\) |

Further analysis of the GAB parameters offered more valuable information about the adsorption and desorption [50]. The non-linear regression technique was adopted, and Eqs. (3) and (4) were substituted into the GAB equation. The characteristic parameters of the GAB model are shown in Table 4. Through the analysis of the experimental results of the sludge drying characteristics, it was found that the drying rate decreased in the later stage of sludge drying. This was consistent with the positive value of \( H_M-H_N \) in the fitting results, which was due to the strong exothermic reaction of water vapour at the main adsorption sites. The adsorption heat of a single-layer water molecule is higher than that of a multilayer water molecule. It is difficult for monolayer water molecules in sludge to separate from the solid surface, which makes the water diffusion rate in the sludge lower than the evaporation rate on the sludge surface and leads to the decrease of the drying rate [55]. The negative value of \( H_L-H_N \) indicated that the condensation heat of single-layer water molecules was lower than that of multilayer water molecules [56]. The enthalpy change of the desorption and adsorption process indicated that the moisture adsorption characteristics of the sludge had a certain degree of irreversibility.

3.3. Net isosteric heat of adsorption

The relationship curve between the net isosteric heat of adsorption (\( q_{st} \)) and the equilibrium moisture content (\( M_e \)) was calculated from the GAB model in Table 2, as shown in Figure 3. The net isosteric heat of adsorption (\( q_{st} \)) had higher values (23.33 and 23.78 KJ/mol, respectively) at a low equilibrium moisture content (\( M_e \)) and decreased rapidly as the content increased. After the equilibrium moisture content (\( M_e \)) reached 25%, the net isosteric heat of adsorption (\( q_{st} \)) gradually approached 0, indicating that the evaporation heat at this time was the same as the latent heat of vapourisation of pure water. A similar phenomenon has been observed by other researchers in foods [40] and agro-products [57]. Water molecules were adsorbed at active polar sites and formed a monolayer in low-moisture sludge. The energy required to remove the water from the layer was higher, but with the formation of a multi-molecular layer, the binding strength of the water molecules and sludge decreased, resulting in the decrease of the net isosteric heat of adsorption (\( q_{st} \)). It was found from the net isothermal adsorption heat change trend that the macroscopic performance of sludge drying was that the drying rate decreased in the middle and later stages of drying due to the strong adsorption of water molecules and sludge, making the drying extremely difficult. On the contrary, when the moisture content was high in the early stage of drying, the water adsorption site decreased, and the adsorption capacity was small, making drying easier. The research conclusions could provide a practical reference for the drying mechanism of sludge. For example, in the later stage of sludge drying, when the moisture content is low, the outward migration rate of water in sludge slows down greatly. At this time, energy can be provided for the drying system via certain methods to maintain the energy demand for the water molecules to separate from the adsorption site; then, the water migration rate can be maintained macroscopically.

3.4. Differential entropy

Differential entropy reflects the magnitude of the force between sludge and water molecules and is directly proportional to the
number of available adsorption sites for water molecules at a specific energy level. According to the solution of the net equivalent heat of adsorption ($q_{st}$), it was brought into Eq. (10) to obtain the relationship curve between the differential entropy ($\Delta S$) and the equilibrium moisture content ($M_e$).

It can be seen from Figure 4 that under certain temperature conditions, the differential entropy ($\Delta S$) decreased as the equilibrium moisture content ($M_e$) increased. When the equilibrium moisture content ($M_e$) increased from 5% to 30%, the variation range of the differential entropy ($\Delta S$) of the desorption process and the adsorption process decreased from 92.95 to 0.15 J/(mol.k) and 76.58 to 1.61 J/(mol.k), respectively. The results showed that when the equilibrium moisture content was low, the number of available adsorption sites was high and decreased as the number of adsorbed water molecules increased. Therefore, sludge can easily absorb water molecules, and sludge drying is difficult at low water content. The results were similar to the results of the isothermal adsorption thermodynamics of soya beans [58].

3.5. Enthalpy–entropy compensation theory

The relationship between the net isotherm of adsorption ($q_{st}$) and the differential entropy ($\Delta S$) was fitted, and their linear relationship under different absolute temperature conditions was obtained (Figure 5).

The experimentally obtained values were satisfactorily correlated by the following expressions:

- Adsorption: $q_{st} = 372.31\Delta S + 1.063$.
- Desorption: $q_{st} = 390.53\Delta S - 0.569$.

The harmonic mean temperature, $T_{hm} = 312.8$ K, in this experiment was calculated using Eq. (9), and the isokinetic temperature ($T_\beta$) at each experimental temperature was obtained by the fitting calculation. It was seen from the fitting results that the isokinetic velocity temperature ($T_\beta$) and the harmonic mean temperature ($T_{hm}$) were not equal, and the enthalpy–entropy compensation theory was established to analyse the energy-driving mechanism of the sludge drying process. The isokinetic temperature, $T_\beta (372.31$ and $390.53$ K), was higher than the harmonic mean temperature, $T_{hm} (312.8$ K), showing that the sludge drying process is mainly driven by enthalpy. The Gibbs free energy is a necessary factor to increase the activity of adsorption sites. The Gibbs free energy ($\Delta G$) of the adsorption process (1.063 KJ/mol) and desorption process (−0.569 KJ/mol) indicated that the adsorption process is not a spontaneous reaction process, whereas the desorption process is a spontaneous reaction process. A similar result for sludge was cited by another author [22].

3.6. Spreading pressure

Spreading pressure refers to the vertical force on any edge area required to prevent the surface of the adsorbed substrate from expanding, and the number of adsorbable points per unit area of the sample is proportional to the spreading pressure value. The relationship between spreading pressure ($\pi$) and water activity ($a_w$) at different temperatures is shown in Figure 6.

The spreading pressure ($\pi$) during sludge desorption had a positive correlation with water activity ($a_w$) at a constant temperature. The spreading pressure ($\pi$) increased as the water activity ($a_w$) increased. However, it decreased as the temperature at a constant water activity ($a_w$) increased and had the same trend with temperature at a constant equilibrium moisture content. The results showed that the increase in water activity ($a_w$) and temperature increased the excess free energy on the surface of the sludge, reduced the activity of the adsorption site and weakened the affinity of water molecules and adsorption sites at the same experimental conditions. Therefore, in the sludge drying process, maintaining a high spreading pressure is beneficial to maintaining a high drying rate. Ouertani and Al-Muhtaerb reached similar research results on wood and beans [59, 60].
3.7. Net integral enthalpy and net integral entropy
The net integral enthalpy represents all available energy and can reflect the strength of the binding of water molecules within sludge with a substrate (i.e. non-aqueous components) during the sludge adsorption (desorption) process. It can provide theoretical information about the energy required during the adsorption process to evaluate the water adsorption capacity of sludge.

The relationship between the net integral enthalpy ($q_{in}$) and equilibrium moisture content ($M_e$) herein under a certain expansion pressure is shown in Figure 7. The net integral enthalpy ($q_{in}$) decreased as the equilibrium moisture content ($M_e$) increased, and the higher the equilibrium moisture content, the lower the net integral enthalpy. Similar trends have been reported in rosemary leaves [23] and black tea [37]. Iglesias attributed this to the multiple layers of water molecules adsorbed on the surface of high-water-content material [48]. A large amount of displacement between the original water molecules and the adsorption site on a solid surface results in a large reduction in the binding energy of the solid surface, which reduces the energy required for the water molecules to migrate away from the adsorption site. This means the sludge surface reduces the demand for environmental energy supply. Therefore, high-water-content drying has a low energy consumption; however, as the drying process proceeds, water molecules in the sludge migrate outward, and the water molecules adsorbed on the surface of the sludge gradually change from multiple layers to single layers. Simultaneously, because of the shrinkage of the sludge structure, the distance between the water molecules and adsorption sites on the surface of the sludge gradually decreases, and the binding energy of the sludge surface is greatly improved.
As can be seen in Figure 7, the net integral enthalpy for adsorption varied from 35.55 to 10.89 KJ/mol in the equilibrium moisture content range of 3.29%–15.65%. Similarly, the net integral enthalpy for adsorption varied from 37.77 to 12.05 KJ/mol in the equilibrium moisture content range of 3.33%–15.26%. For both processes, desorption ($q_{\text{in}}$) was higher than adsorption ($q_{\text{in}}$), which may have been caused by the irreversible expansion of the adsorption process.

Net integral entropy ($\Delta S_{\text{in}}$) is related to the gravity, repulsion and spatial layout of sludge and water molecules. It can describe the randomness and disorder of water molecules in sludge at the micro level and quantify the molecules’ mobility.

The variation in net integral entropy ($\Delta S_{\text{in}}$) with the equilibrium moisture content ($M_e$) under different temperature conditions is shown in Figure 8. At a low equilibrium moisture content ($M_e$), the net integral entropy ($\Delta S_{\text{in}}$) decreased as the equilibrium moisture content ($M_e$) increased, and the entropy of desorption was lower than that of adsorption. With the adsorption of water, the net integral entropy of desorption reached the lowest points at the equilibrium moisture contents of 2.99%, 3.41% and 3.78%, i.e. $-93.17$, $-98.34$ and $-93.28$ KJ/mol, respectively, and then increased gradually. Similar trends have been reported in the literature for safflower petals and tarragon [61] and carboxymethyl cellulose, guar, locust bean, tragacanth and xanthan gums [62]. The initial decrease indicated that the existing adsorption sites tended to be saturated. At the single molecular layer, the adsorption of the strongest adsorption sites hindered the movement of the water molecules. With the emergence of multilayer water molecules in water adsorption, the adsorption water beyond the critical water content increased the net integral entropy. It can

Figure 7. Relationship of net integral enthalpy of sludge $q_{\text{in}}$ with equilibrium moisture content $M_e$: (a) adsorption and (b) desorption.

Figure 8. Relationship of net integral entropy of sludge $\Delta S_{\text{in}}$ with equilibrium moisture content $M_e$: (a) adsorption and (b) desorption.
be seen from Figure 8 that the net integral entropy was negative because the structure of the adsorbent itself changed during the experimental process [61]. At 303 K, the rising speed of the net integral entropy was faster than that at other temperatures and maintained a negative value, indicating that a low temperature could weaken the structural change.

4. CONCLUSIONS

In the study, wastewater sewage sludge moisture sorption characteristics were conducted experimentally at 303 K, 313 K and 323 K using of static gravimetric method. The experimental data were analysed using eleven mathematical models. The thermodynamic parameters of the sludge including the net isosteric heat of adsorption ($q_m$), differential entropy ($\Delta S$), spreading pressure ($\pi$), net integral enthalpy ($q_{in}$) and net integral entropy ($\Delta S_m$) can be used to promote the wastewater sewage sludge disposal and to improve the sludge drying process with a comprehensive drying model. The following conclusion can be drawn from the results:

(1) At a certain temperature, the equilibrium moisture content of wastewater sewage sludge has a positive correlation with water activity. With certain water activity, the equilibrium moisture content of wastewater sewage sludge decreases as the temperature increases, and high temperatures will reduce the sludge’s hygroscopicity.

(2) The adsorption isotherm of wastewater sewage sludge is a typical type II curve, and the best model to describe the isotherms of the sludge’s desorption and adsorption is the GAB model. It has the highest $R^2$ (0.9989) and the lowest SSE ($9.946 \times 10^{-5}$). The predicted values from the model agree well with the experimental values.

(3) Through the analysis of the relationship between the net equal adsorption heat of wastewater sewage sludge and the equilibrium moisture content, it was found that the value in the later stage of drying is larger, the energy required for water molecules to desorb from the adsorption site is higher and the drying rate is reduced. Therefore, in the later stage of sludge drying, when the moisture content is low, the water migration rate inside the sludge is greatly slowed down. At this time, energy can be provided to the drying system via a certain method to keep the water molecules from the adsorption site, macroscopically maintaining the moisture migration rate.

(4) The difference between the harmonic average temperature and the isokinetic temperature verifies the enthalpy entropy compensation theory and concludes that the adsorption process is a non-spontaneous reaction driven by enthalpy.

(5) The spreading pressure values of wastewater sewage sludge increase as the water activity increases and decrease as the temperature increases at constant water activity. During the drying process, the temperature should be increased appropriately so that the moisture is quickly removed.

(6) The decrease of net integral enthalpy with equilibrium moisture content indicates that the bond strength of water and solid decreases. At 303 K°C, 313 K313 K and 323 K, net integral entropy decreases to a minimum value as the moisture content increases at 0.0299, 0.0341 and 0.0378, respectively, and then increases.

4. CONFLICTS OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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