INTRODUCTION

The patterns of everyday activities tend to produce a large amount of waste which is processed by sophisticated technologies later on. In this regard, water treatment has been occupying a significant place on the environmental agenda of developed countries, especially as wastewater discharges have considerably evolved.

In Morocco, especially in the Marrakech-Safi region, the pollution caused by the sludge discharge from drinking water treatment plants has reached an estimated quantity of 5.5 tons per day. However, the treatment issue is often not considered in terms of the parameters related to water treatment. Consequently, the daily production rates of the wastewater sludge constituted a potential threat to the environment (Fantasse et al., 2020).

In this paper, a thermodynamic analysis of DWTS wastes was conducted based on the isosteric heat and compensation theory. Different results concerning the mineralogical identification of sludges were established. Findings revealed that the by-product of water purification was mainly composed of aluminum, silica and iron hydroxides, with pH varying between 6.23 and 6.85. The suspended matter was between 18.3 and 19.6 m/l. The volatile matter of the three sludge samples was between 18 and 21%. The measured dry matter content was between 13.41 and 15.23%. The experimental tests were performed under temperatures from 45 and 60 °C, the experimental data of the sorption curves were fitted by using several models of correlation. Furthermore, the analysis showed that the Peleg’s model perfectly described the isotherm curves in the activities ranging from 0 to 90%. The net isosteric heats of sorption of the three hydroxide sludge from the Moroccan treatment station: $S_k$, $S_m$ and $S_s$, were determined for desorption and adsorption. Moreover, it was revealed that the equilibrium water content rising lead contributed to the reduction of the net isosteric heat and the entropy of sorption. Finally, the enthalpy-entropy compensation showed that the sorption mechanism involved was enthalpy driven.

Keywords: drinking water sludge, sludge valorization, wastewater management, thermodynamic analysis, isosteric heat.

Thermodynamic Analysis and Mathematic Modeling of Waste Sludge from Drinking Water Treatment Plants

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ABSTRACT

Water treatment annually produces a huge amount of Drinking Water Treatment Sludge (DWTS) wastes. The latter causes environmental problems in Morocco in terms of energy and pollution. Therefore, cost-effective and eco-friendly solutions for managing them should be proposed in order to reduce the frequency of storage along with transportation costs. In this paper, a thermodynamic analysis of DWTS wastes was conducted based on the isosteric heat and compensation theory. Different results concerning the mineralogical identification of sludges were established. Findings revealed that the by-product of water purification was mainly composed of aluminum, silica and iron hydroxides, with pH varying between 6.23 and 6.85. The suspended matter was between 18.3 and 19.6 m/l. The volatile matter of the three sludge samples was between 18 and 21%. The measured dry matter content was between 13.41 and 15.23%. The experimental tests were performed under temperatures from 45 and 60 °C, the experimental data of the sorption curves were fitted by using several models of correlation. Furthermore, the analysis showed that the Peleg’s model perfectly described the isotherm curves in the activities ranging from 0 to 90%. The net isosteric heats of sorption of the three hydroxide sludge from the Moroccan treatment station: $S_k$, $S_m$ and $S_s$, were determined for desorption and adsorption. Moreover, it was revealed that the equilibrium water content rising lead contributed to the reduction of the net isosteric heat and the entropy of sorption. Finally, the enthalpy-entropy compensation showed that the sorption mechanism involved was enthalpy driven.

Keywords: drinking water sludge, sludge valorization, wastewater management, thermodynamic analysis, isosteric heat.
and water characteristics (Bourioug et al., 2015). These processes combine the chemical actions of reagents with physical actions.

In order to facilitate the deposition of particles at the bottom of the basin, the decantation stage can be coupled with two chemical steps to combine the particles and make them heavier; the first step is clotting. This step can be conducted by the addition of the iron or aluminum salts to water to reduce the electrostatic forces of repulsion between the particles, and thus allow them to coagulate (Benlalla et al., 2015). The second step is flocculation whereby water is slowly stirred, allowing the particles to clump together and form larger clumps. Their high mass allows them to settle more quickly at the bottom of the basin under the effect of gravity (Benlalla et al., 2015; Chahid et al., 2015).

The identification of the hygroscopic character of hydroxide sludge, which is an important step for further treatment and recovery, requires the characterization of sorption isotherms linking the equilibrium water content, for a given temperature, and the relative humidity of the environment surrounding the product (Gu et al., 2021). It is a function of numerous interactions at the microscopic scale, produced between the solid skeleton and the water molecules.

The variation of the quality or composition of the material causes changes in its sorption isotherms. Due to the complexity of the sorption phenomena, the sorption isotherms cannot be predicted based on a theoretical analysis. Therefore, experimental tests should be established for each sample (Idlimam et al., 2008). The thermodynamic analysis curves provide the information on the distribution and the intensity of water molecule bonds, as well as their functional availability in the biochemical and biological substances (Abdenouri et al., 2010; Gu et al., 2021). The determination of the moisture sorption characteristics of this sludge would be helpful to specify the conditions of transport and storage. In addition, they will be used to predict the shelf life (Abdenouri et al., 2010; Onyelowe et al., 2019).

This study focused on the contrast between the water transfer in different types of hydroxide sludge and the thermodynamic properties in hygroscopic equilibrium. The following points were studied from experimental data:

- The mineralogical analysis of three hydroxide sludge.
- The equations of isosteric heat as a function of the equilibrium water content of the drinking water sludge.
- The differential entropy, isokinetic temperature and Gibbs free energy of the three samples.
- The enthalpy-entropy compensation that thermodynamically manifests the structuring and destruction of water.

MATERIALS AND METHODS

Sludge samples and origin

The DWTS amount generation depends on seasons as well as climatic conditions (precipitation, thunderstorms, etc.). The total aluminum sulfate (estimated at 2500 tons/year (Chahid et al., 2015) and used in the clotting phase during water clarification) is stored by sludge at the end of the treatment cycle. The sampling of this sludge was carried out at the level of the liquid sample called Fresh Sludge (FS) and collected at the level of the decanter purges. The sludge samples were prepared and then tested for chemical and mineral characterization.

Mineralogical properties

The present study was mainly concerned with three drinking-water treatment plants located in Marrakesh, Elkelaa des Sraghna, and Safi cities. Three sampling campaigns were carried out at the three stations in sludge-bed decanters during the months of March and April 2019. The main parameters of the three sludge samples were analyzed using the different physicochemical and microbiological analytical methods described in Table 1.

Table 1. Used methods of mineralogical parameters.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Used method</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Ph Metry</td>
<td></td>
</tr>
<tr>
<td>Suspended matter (SM)</td>
<td>Membrane filtration</td>
<td>mg/l</td>
</tr>
<tr>
<td>Volatile matter (VM)</td>
<td>Incineration at 550°C</td>
<td>%</td>
</tr>
<tr>
<td>Dry matter (DM)</td>
<td>Drying technique</td>
<td>%</td>
</tr>
<tr>
<td>Moisture content (MC)</td>
<td>Gravimetric statique</td>
<td>%</td>
</tr>
</tbody>
</table>

Thermodynamic study

Water activity

Water activity ($a_w$) is the measure of the degree of liberty of the water-retained hygroscopic product. It is defined as in Equation (1):

$$ a_w = \frac{P_{wp}}{P_{vs}} = \frac{HR(\%)}{100} $$

(1)
where: \( P_v \) – water vapour partial pressure in air (Pa), 
\( P_{sv} \) – the saturated vapor partial pressure (Pa),
\( \text{RH} \) – the relative humidity of air (%).

**Sorption residue**

The sorption residue (\( e_i \)) is calculated by the following equation:

\[
e_i = X_{eqi,exp} - X_{eqi,pre}
\]  

Equation (2) is used to compare the models of correlation in order to discover which model provides the closest residual sorption error to the origin line, based on the correlation coefficient (r) and the Mean Standard Error (MSE). Table 2 shows the selected models used to fit the sorption isotherms of the sludge (Idlimam et al., 2008; Mohamed et al., 2005; Peleg, 1993).

The analytical expressions of these models are listed in Table 2. These expressions depend on water activity (\( a_w \)), moisture content \( X_{eq} \) (dry basis), temperature \( T \) (°C), and other several constants (A, B, C, D, \( K_1 \), and \( K_2 \)).

**Net isosteric heat and entropy determination**

The net isosteric heat of sorption (sorption enthalpy) is the energy required to free the molecules of bound water from the solid skeleton. It is calculated from the sorption isosters. The curve giving \( \ln(a_w) \) versus \( 1/T \) at a constant water content according to the following Equation (9) (Idlimam et al., 2008).

\[
\ln(a_w) = -\frac{\Delta h_d}{R} \frac{1}{T} + \frac{\Delta S_d}{R}
\]  

From the slope of the isosters and for each \( X_{eq} \) water content, it is possible to deduce the corresponding net isosteric heat and trace the \( \Delta h_d=f(X_{eq}) \) curve.

The entropy measures the degree of disorder at a microscopic level (Gu et al., 2021; Štrkalj & Malina, 2011). Higher entropy means higher disorder of water molecules. In fact, the typical surface of the product has a very important role for determining the binding properties between water and the sample. Indeed, entropy measures the homogeneity of the system at a microscopic level. Each molecule is elastically linked to its neighbors and vibrates around a fixed average position (Cervantes et al., 1994). As a result, the position and energy of each particle are random.

The \( \Delta h_d \) and \( \Delta S_d \) values for sorption and desorption, at given moisture contents, are calculated by a linear regression equation using Equation (9).

**Enthalpy-entropy compensation**

The compensation theory confirms that there is a linear relation between the isosteric heat and entropy. The enthalpy-entropy compensation process thermodynamically manifests the structuring-destruction of water, Equation (10) (Gu et al., 2021; Mohamed et al., 2005):

\[
\Delta h_d = T_\beta \Delta S_d + \Delta G_\beta
\]  

where: \( T_\beta \) is the isokinetic temperature (K) and \( \Delta G_\beta \) is the Gibbs enthalpy (J/mol).

**RESULTS AND DISCUSSION**

**Analysis of mineralogical sludge compositions:**

The obtained results were explained and analyzed, and a summary of the physicochemical as well as microbiological and analytical methods used was presented below.

**The mineralogical characterization**

The mineralogical characterization showed that the three samples of hydroxide sludges were
mainly composed of the following rate of constituents: SiO$_2$ (47.77–45.21%), Al$_2$O$_3$ (27.08–25.69%), Fe$_2$O$_3$ (10.31–8.96%), CaO (4.41–3.4%), MgO (3.91–2.45%) and K$_2$O (2.2–1.97%).

The presence of the high level of aluminum oxide was due to the use of alumina sulfate as a coagulant in the water purification process. The low CaO content coming from clay with a low limestone content indicated that the sludge studied consisted mainly of silico-aluminous clay.

**pH measurement**

The purpose of pH measurement was to indicate the acidity or alkalinity of the raw sludge. The results of the pH measurement indicated the values between 6.23–6.85. This is consistent with the literature, as the sludge from drinking water was very rich in organic matter, which is acidic (Bentahar et al., 2016).

**Suspended material**

The presence of the suspended matter in significant concentration influenced the physico-chemical and biological characteristics, which were reflected in the nature of the sludge treatment which was between 18.3 and 19.6 m/l.

**Volatile matter**

The rate of volatile matter is an important factor in identifying the capacity of the sludge to undergo recovery treatment such as dewatering or incineration. The results obtained for the presence of volatile matter in sludge samples varied between 18 and 21%. This low VM content (less than 30%) made the sludge easy to thicken and dewater.

**Dry matter**

In order to determine the dryness of the sludge, the dry matter concentration parameter DM was used. The dry matter DM content measured in the three raw sludge samples $S_k$, $S_s$, and $S_m$ ranged from 13.41 to 15.23%.

**Thermodynamic analysis**

**Experimental results of equilibrium moisture content**

The equilibrium of moisture contents as a function of the water activity of the DWTS of the three samples $S_k$, $S_s$, and $S_m$ are shown in Figure 1. The experimental results for the adsorption and desorption of the three samples were obtained for the temperatures 45°C and 60°C.

The effect of the temperature was significant on both the adsorption and desorption isotherms for the full range of water activities ($a_w$). The effect of temperature on the adsorption and desorption isotherms was remarkable over the whole range of water activities. Indeed, for a high temperature state, the excitation of the molecules was important, resulting from lower attraction forces among water molecules (Mghazli et al., 2016). The introduction of water vapor $X_{eq}$ increased along with the decreasing of temperature, as well as the moisture content was relatively low at low water activities, which also gradually increased with the relative humidity of ambient air. Therefore, the moisture content at equilibrium depended upon the temperature and the ambient air (Ashour et al., 2011; Mghazli et al., 2016).

Figure 1. Adsorption and desorption of the three sludge samples
The mathematic modeling of the isotherms of desorption and adsorption was used to advance our understanding of the mechanisms involved in the sludge. The comparison between the models was conducted according to their coefficient (r) and their MSE. The results of the experimental data at a temperature of 45°C were shown in (Figure 2), the comparison adjusted by the used models showed that the Peleg model is the most suitable to describe the equilibrium water content of the three samples (S_k, S_s, and S_m).

Table 4 shows two models chosen from the seven studied in order to fit the adsorption (a) and desorption (b) of the three sludge samples. The Peleg model was found to be the most appropriate model to describe the total hygroscopic equilibrium of sludge (see Figure 2), with r values between 0.9984 and 0.9995, the MSE between 0.1203 and 0.5957 in the case of adsorption. For adsorption the r value was between 0.9993 and 0.9998, the MSE between 0.2978 and 0.6419, the relative humidities between 0.05 and 0.9.

On the basis of the residual errors that are illustrated in Figure 3 for desorption and adsorption, it was revealed that the experimental data and predicted values by the models were nearly identical. The residuals errors were found to be less than 1%. The analysis of residue values in relation to the mean standard error values (MSE) showed the coincidence with previous results (Table 4).

The calculation of residual sorption isotherms of the three samples estimated by the seven models was performed to discover whether the difference residues were minimal between experimental data and predicted values by these models or not. The residual error was calculated by the Equation (2). The sorption dependence on temperature was well-observed. The sorption capacity decreased as the temperature increased. This caused a break in the water binding sites when the equilibrium moisture content is decreased.

**Isosteric heat and the compensation theory**

The sorption heat (released during the sorption process of water vapor molecules on a surface of the adsorbent) provided an indication of the water state as well as the interaction between molecules and adsorbent materials. Moreover, it was used for the calculation of the energy consumption.

Figure 4 illustrates the sorption isosters of the DWTS samples (S_s, S_k, and S_m). It showed that the isosteric heat was high for low water content values. This was due to the strong binding of water to the material, which became negligible compared to the residual heat at high humidity. The significant decrease in isosteric heat for low water contents in the product was due to the presence of polar zones of high activity which were coated with water molecules forming the monomolecular layer. The increase in the intensity of the interaction between water and the sample structure at low moisture content also indicates the high resistance to water movement from the interior to the surface of the samples.

In general, the vaporization of a water molecule requires a value of heat which equals the sum of the latent heat \(L_{vap}\) and the isosteric sorption heat \(Q_s\). The increase in the moisture content at the equilibrium, as indicated in Figure 5, can cause the decreasing in the net isosteric heat. This finding was due to the strong binding of water in the sludge of S_k and S_s. However, the binding was
weak in the case of S_m in the adsorption. For the desorption, it was noticed that the sludges S_k and S_m had a higher net isosteric heat compared to that of S_s because of the structure inside the sludge where there was water that built a single layer that may differ from one sludge to another. This energy appeared only in the hygroscopic domain and became significant with regard to the evaporation energy only for very low water contents.

This phenomenon is explained by the fact that in a very small area of moisture, where the water content increases, many products inflate and enhance the opening of new adsorption sites for strong bonds, which increases the isosteric heat. The structuring-destruction of water was thermodynamically manifested by the enthalpy-entropy compensation process. In this regard, Figure 6 illustrates the enthalpy-entropy compensation

Table 4. Two selected models used to fit the adsorption (a) and desorption (b) of the three samples sludge

<table>
<thead>
<tr>
<th>Adsorption</th>
<th>Henderson</th>
<th>Peleg</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>45°C</td>
</tr>
<tr>
<td>S_k</td>
<td>A</td>
<td>1.86</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>-</td>
</tr>
<tr>
<td>r</td>
<td>0.9821</td>
<td></td>
</tr>
<tr>
<td>MSE</td>
<td>0.5831</td>
<td></td>
</tr>
</tbody>
</table>

| S_s        | A   | -0.05 | -0.13 | -0.12 | 29.25 | 10.78 | 31.96 |
|           | B   | -0.78 | -0.93 | -0.97 | 5.64 | 65.95 | 5.49 |
|           | C   | 0.78 | 1.077 | 1.10 | 7.33 | 1.43 | 8.62 |
|           | D   | -   | -   | -   | 0.83 | 17.5 | 0.84 |
| r         | 0.9978 |       |       |       |       | 0.9995 |
| MSE       | 0.5398 |       |       |       |       | 0.2966 |

| S_m        | A   | -0.06 | 0.519 | 0.12 | 7.44 | 4.14 | 25.25 |
|           | B   | -0.77 | 0.12 | -0.48 | 37.69 | 21.96 | 11.72 |
|           | C   | 0.85 | -0.61 | 0.38 | 1.10 | 0.85 | 11.91 |
|           | D   | -   | -   | -   | 9.15 | 4.71 | 1.74 |
| r         | 0.9978 |       |       |       |       | 0.9984 |
| MSE       | 0.5582 |       |       |       |       | 0.5957 |

<table>
<thead>
<tr>
<th>Desorption</th>
<th>Henderson</th>
<th>Peleg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>45°C</td>
</tr>
<tr>
<td>S_k</td>
<td>A</td>
<td>2.01</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>19.23</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>8.24</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>-</td>
</tr>
<tr>
<td>r</td>
<td>0.9773</td>
<td></td>
</tr>
<tr>
<td>MSE</td>
<td>1.13503</td>
<td></td>
</tr>
</tbody>
</table>

| S_s        | A   | 1.4934 | 0.8455 | 1.0662 | 0.6076 | 0.1110 | 1.2071 |
|           | B   | -0.04 | -0.09 | -0.11 | 8.15 | 35.73 | 6.62 |
|           | C   | -0.54 | -0.74 | -0.84 | 24.18 | 9.40 | 32.72 |
|           | D   | -   | -   | -   | 0.95 | 11.24 | 0.87 |
| r         | 0.9973 |       |       |       |       | 0.9998 |
| MSE       | 0.5935 |       |       |       |       | 0.4544 |

| S_m        | A   | 0.4571 | 0.632 | 0.691 | 0.463 | 0.371 | 0.529 |
|           | B   | -0.085 | -0.11 | -0.11 | 8.56 | 43.77 | 7.61 |
|           | C   | -0.61 | -0.75 | -0.78 | 34.25 | 9.20 | 39.18 |
|           | D   | -   | -   | -   | 0.85 | 11.97 | 0.86 |
| r         | 0.9955 |       |       |       |       | 0.9995 |
| MSE       | 0.8468 |       |       |       |       | 0.2978 |
phenomenon that appeared in the sludge; the desorption values was greater than those of adsorption with a clear trend of the product. A linear relationship with a correlation coefficient \( r \) that is approaching to 1 is shown in Figure 6. This result indicated the existing of the compensation phenomenon. Furthermore, it is possible that they were caused by the differences in the structure of water around the periphery of the product both before and after sorption. The understanding of the changes in the isosteric heat and the differential entropy are interesting. This parameter showed a strong relationship with the equilibrium moisture content.

On the basis of the theory of enthalpy-entropy compensation, it should be noted that the linear correlation between isosteric heat and entropy for a specific moisture value was determined by the Equation (10).

Figure 6 shows the verification of the compensation process for three samples. The linear regression was accomplished on the thermodynamic data in order to determine the isokinetic temperature and the Gibbs free energy values. The findings are listed in Table 5.

The sign value of Gibbs free energy \( (\Delta G) \) indicated the nature of the
Figure 4. Isosters of adsorption and desorption of the three drinking water sludges samples Sk, Ss and Sm

Figure 5. Net isosteric heat of desorption and desorption
adsorption-desorption process: spontaneous ($\Delta G^\beta < 0$) or non-spontaneous ($\Delta G^\beta > 0$). On the basis of the data in Table 5, it was noticed that the adsorption was non-spontaneous for the three samples; however, desorption was spontaneous. Isokinetic temperatures of all the samples and for both desorption and adsorption varied from 311 to 399 K.

**CONCLUSIONS**

This paper aimed at optimizing drinking wastewater sludge using a thermodynamic approach. A characterization analysis of sludge from three drinking water treatment plants was performed in order to reduce their management for low-cost. The sludges were mainly composed of aluminum oxide, silica, iron and potassium. The results of the pH measurement ranged from 6.23 to 6.85. The presence of the suspended matter in the three sludges was between 18.3 and 19.6 m/l. The volatile matter in sludge samples varied between 18 and 21% (less than 30%), that made the sludge easy to thicken and dewater. The measured dry matter content in the three raw sludge samples $S_k$, $S_s$, and $S_m$ ranged from 13.41 to 15.23%. The residual errors for desorption and adsorption of the three samples showed that the experimental data and predicted values by the models were nearly identical. The found residuals errors were less than 1%. The application of the Claisis-Clapeyron equation has made it possible to evaluate the net isosteric heat. In addition, the differential entropy of the three studied sludge samples were expressed and controlled satisfactorily according to the water content. Their decrease was proportional to the increase of the moisture content. The evaluation of the enthalpy-entropy compensation theory was proven successfully for the three drinking water sludge samples with a clear linear trend. The thermodynamic analysis of drinking water treatment sludge, namely enthalpy, free energy and entropy, are an essential step in the study of all drying processes, in order to determine the final water contents, which in turn serve to optimize the drying conditions of hydroxide sludge, for the purpose of ensuring its storage. Moreover, it was a preliminary phase in a subsequent step of a study in order to evaluate the drying kinetics of a thin-layer convection of hydroxide sludge in a solar convective dryer.
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