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Determining Water Content in Waste Sludge Cake by Time-Domain NMR

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Abstract

The application of low-field time-domain nuclear magnetic resonance (TD-NMR) to measure water content and assess the distribution of water fractions in sludge samples has been investigated. The results of TD-NMR measurements on 26 dewatered sludge samples revealed a strong correlation between sludge water content and key features of the T_2 distribution curves, including the maximum relaxation time and peak area, demonstrating the potential of the TD-NMR method for estimating sludge moisture content. We have not observed a direct relationship between the peaks in T_2 relaxation distribution curves obtained by Inverse Laplace Transform (ILT) and the expected water fraction ratios, apparently because sludge structure is highly variable from sample to sample. Despite the bio-complexity of sludge samples, the direct correspondence between key features of the T_2 relaxation curves and moisture content demonstrates the high potential of TD-NMR as a tool for controlling sludge moisture content, even in an online device configuration.

Keywords: TD-NMR; relaxation time; waste sludge; moisture; water fractions

1. Introduction

Wastewater treatment plants produce significant volumes of sludge, which is a complex mixture of water, organic and inorganic solids, microorganisms, and pollutants. Dewatered waste sludge characterization reveals complex pollution properties, including high moisture content (70–85%) and the material is chemically and physically heterogeneous, containing inorganics, proteins, lipids, extracellular polymeric substances, pathogens, heavy metals, and persistent organic pollutants [1,2].

Generally, water in dewatered sludge cake can be categorized into three types: free water, interstitial water, and bound water. Free water refers to unbound moisture between sludge particles and typically accounts for 65–85% of the sludge's total water content. Unlike bound water, it does not adhere directly to solid surfaces and is therefore more easily separable. This fraction is the primary target of sludge thickening, as it can be partially removed by gravity settling under controlled conditions with sufficient residence time in thickeners. Interstitial water is defined as the water occupying the void spaces between sludge flocs and constitutes approximately 10–25% of the total sludge water content. Its mobility is restricted by surface tension, which limits its redistribution across solid particle surfaces. As a result, its removal requires substantial mechanical energy input, typically achieved through processes such as vacuum filtration or centrifugation. Bound water (BW) consists of water molecules entrapped within extracellular polymeric substances (EPS) and intracellular compartments, accounting for approximately 10% of the total sludge water content. Due to strong molecular interactions, mechanical dewatering is largely ineffective for this fraction.

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Instead, BW and intracellular water must be converted into free water through EPS modification or cell membrane disruption. To remove this fraction, common approaches include chemical coagulation, biological treatment, thermal processing, and oxidative methods [3–11]. Therefore, understanding the distribution of different water fractions is critical for improving sludge dewatering efficiency and selecting appropriate conditioning or pre-treatment strategies. As discussed above, different water fractions require different pre-treatment approaches to enhance the effectiveness of the dewatering process. However, conventional moisture measurement methods do not provide insight into the distribution of water fractions within sludge.

Nuclear magnetic resonance (NMR) is a well-known technique for the characterization of organic materials. High-resolution NMR spectroscopy, also known as high-field (HF) NMR, is routinely preferred due to the rich information it provides about the examined chemical structures. This technique is widely used as a research and analytical tool in biology, chemistry, medicine, and materials science. However, the application of this technique involves high device and operational costs due to advanced equipment, cryogenic cooling, a superconducting magnet, and the need for highly qualified personnel to analyze the acquired NMR data. These requirements significantly limit the practical applicability of NMR spectroscopy, especially in mobile and small laboratories. There is a much lower-cost version of this technique. This method is known as time-domain NMR (TD-NMR), which does not probe spectral information but rather provides relaxation parameters of the measured substance. Because a highly uniform magnetic field is not required, TD-NMR is usually based on permanent magnet technology, with no cryogenic system required. Magnetic fields produced by permanent magnets are usually much lower than those due to superconducting magnets; therefore, it is sometimes called low-field NMR. It is less expensive, easier to use, and allows for portable configurations. Therefore, TD-NMR is particularly attractive for quality control, industrial monitoring, and field-based applications. In this technique, materials are characterized by measuring the relaxation times of the samples rather than the NMR spectra. Consequently, TD-NMR has become a valuable analytical tool in many scientific and technological fields. It is also considered one of the well-established methods for characterizing porous, heterogeneous, and semi-liquid materials. In food science, it is used to analyze water content and distribution in food products, supporting quality control and shelf-life estimation [12]. In agriculture, it plays a crucial role in monitoring soil moisture and plant hydration, aiding in effective water management strategies [13]. Furthermore, in materials science, TD-NMR helps assess the porosity and moisture content of polymers and composite materials [14]. It has been shown that TD-NMR is useful for tracking the moisture content in sludge [5]. As a non-destructive and rapid measurement technique, it offers several advantages. It facilitates efficient sample preparation with minimal pre-treatment while enabling multiple analyses of the same sample [5,8]. However, the application of TD-NMR for determining sewage sludge moisture is still an active area of research, as appropriate methods for analyzing TD-NMR data have not yet been established. In particular, the inherent heterogeneity of sewage sludge necessitates a more thorough and nuanced understanding of its water content to improve measurement accuracy and reliability. The interpretation of TD-NMR results for heterogeneous sludge samples, specifically the spin-spin and spin-lattice relaxation curves, requires a certain level of expertise. In this context, Inverse Laplace Transform (ILT) analysis is commonly employed to determine the distribution of relaxation times within measured samples. It is usually stated that ILT enables quantification of different forms of water in sludge, including bound, capillary, and free water. However, additional research is still required to refine the methodology for TD-NMR measurements to assess sludge water content. This includes developing suitable analytical and quantification techniques to enhance accuracy and reliability.

In this study, TD-NMR measurements were performed on sludge cake samples collected from a wastewater treatment plant (WWTP) under varying operational conditions and classified into three categories based on their operational and dewatering characteristics to evaluate the effectiveness of TD-NMR in distinguishing water fraction distributions and estimating moisture content. Spin-spin (T_2) relaxation decay curves were obtained from sludge samples using the Carr-Purcell-Meiboom-

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Gill (CPMG) sequence. The T_2 distributions for a set of the sludge samples were extracted using the Inverse Laplace Transform (ILT).

2. Materials and Methods

2.1. Sludge Sampling

Sludge samples were collected from the decanter centrifuge effluent, also known as cake, at an urban wastewater treatment plant serving a population of 670.000 inhabitants, which employs advanced biological treatment, including biological phosphorus and nitrogen removal.

Sludge samples were collected from the WWTP dewatering unit effluent under varying conditions to represent three categories and evaluate the effectiveness of TD-NMR in distinguishing water-fraction distributions. In addition, some of the dewatered sludge samples were subjected to further laboratory centrifugation at 11,000 rpm for durations ranging from 15 to 75 minutes to remove available free water.

The sludge samples were grouped into three categories:

✓ Inefficient dewatering: samples collected during non-steady-state operation and/or after water addition.

✓ Relatively efficient onsite dewatering: samples collected during steady-state operation.

✓ Highest dewatering performance (laboratory centrifugation): samples subjected to additional dewatering under controlled laboratory conditions.

Reference moisture content was determined using the gravimetric method described in Standard Methods 2540B [15]. Approximately 10 g of each sludge sample was dried in a laboratory oven at 105 °C for 24 h until a constant weight was achieved. All measurements were performed in triplicate. The water content (W, %) of the sludge samples was calculated using the equation $W=(M_1-M_2)/M_1\times100\%$, where M_1 represents the initial mass of the sludge sample and M_2 denotes the mass of the sample after drying to a stable residual weight. In total, 26 waste sludge samples with moisture contents ranging from approximately 74% to 85% were analyzed by TD-NMR.

2.2. Sludge Characterization

The moisture content for three groups of sludge samples is summarized in Table 1. Water content in the first group samples ranged from 81.1% to 85.3%, with an average of 83.1 ± 1.37%. For the second group of samples, water content ranged from 77.8% to 80.8%, with an average of 79.2 ± 1.02%. The samples in the third group had water contents ranging from 74.4% to 76.6%, with an average of 75.4 ± 0.96%. The variability in moisture content among the sample groups is shown in Figure 1. As shown in the figure, three groups span the entire water-content range from 74.4% to 85.3%, with the lowest variability observed in the group with the highest dewatering performance and the highest one in that with inefficient dewatering.

Table 1. Moisture content ranges for various groups of the sludge samples.

Sample group	n	Min-Max, %	Mean ± Standard Deviation, %
Samples representing inefficient dewatering	12	81.1-85.3	83.1 ± 1.37
Samples representing efficient dewatering (on-site)	8	77.8-80.8	79.2 ± 1.02
Samples representing the highest dewatering performance (further centrifuged in a laboratory)	6	74.4-76.6	75.4 ± 0.96

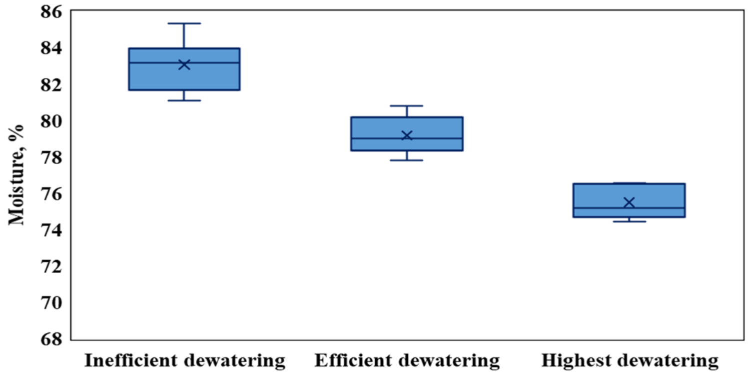

Figure 1. Distribution of water content in sludge samples for various dewatering groups.

2.3. TD-NMR Experiments

The Bruker Minispec mq20 TD NMR device was used for obtaining relaxation curves of sludge samples. The samples were placed in 20 mm NMR quartz tubes and preconditioned at 25 °C. Afterward, the samples were placed in the NMR device and allowed to equilibrate for at least 10 minutes before each measurement. The Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was used to obtain spin-spin relaxation curves. For accurate post-processing of the measured signal, the signal-to-noise ratio (SNR) should be high enough. For that reason, each measurement was repeated 5 times for each sample, and the average of these measurements was used for analysis. The delay time between successive measurements was chosen to be roughly 5 times greater than the observed T_1 value to prevent saturation of the NMR signal. To check the effect of self-diffusion on the analyzed data, different echo times were tested in CPMG measurements. The echo time was set to 200 μs to minimize the influence of the diffusion term. The CPMG measurement parameters applied in the experiment are given below in Table 2.

Table 2. CPMG parameters.

Parameters for CPMG	Unit
B_1 Frequency	19.95 MHz
90° Pulse Amplitude	3 dB
180° Pulse Amplitude	9 dB
Echo Time	200 μs
Number of Echoes	5000
Repetition Time	5000 ms
90° Pulse Length	3.16μs
180° Pulse Length	6.06 μs
Receiver Gain	53 dB
Number of Scans	4

2.4. Analysis of TD-NMR Data

The distribution of the T_2 relaxation constant has been obtained by the Inverse Laplace Transform (ILT) procedure. For ILT analysis, the non-negative least squares (NNLS) routine in the PROSPA software package of the KEA-2 NMR console (Magritek Inc.) was used. In the simplest consideration of a single discrete value of relaxation time T_2, an experimental signal A(t), measured in a CPMG pulse sequence, is defined as:

$$A(t) = A(0)\exp(-t/T_2) \quad (1)$$

where t is the time variable of the acquired signal, and T_2 is the single-valued relaxation time. For a case of multiple relaxation times, we can suppose the discrete set of exponents:

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$$A(t) = \sum_i^k A_k(0)\exp\left(-\frac{t}{T_{2i}}\right) \quad (2)$$

where k is a number of characteristic exponents in the CPMG relaxation curve. In the above consideration, the discrete set of the components $A_k(0)$ can be viewed as a spectral component represented by delta-function of $A_k(0)\delta(T_2 - T_{2k})$ in the continuous spectra consideration (see the Eq.3 below).

For comparison purposes, we also applied least-mean-square fitting to the experimental data using a discrete set of exponential decays. We tested three discrete exponents to analyze the relaxation curves of sludge samples and compared these results with the continuous relaxation-time spectrum obtained from NNLS ILT.

The NNLS routine applies regularization to exclude delta peaks (discrete set) with discontinuous points, or negative amplitude values in the distribution $g(T_2)$ of relaxation times T_2, yielding the "smooth" spectrum of the relaxation times. In the consideration, based on a continuous relaxation time spectrum, the TD NMR signal is given as:

$$A(t) = \int g(T_2)\exp\left(-\frac{t}{T_2}\right)dT_2 \quad (3)$$

where $\exp(-t/T_2)$ is the kernel function of the system. It should be noted that NNLS provides a quasi-continuous distribution, because the time-domain measurements yield a discrete set of 2N points rather than a continuous curve: an experimental TD NMR signals A(t) is a set of n data points acquired over the time interval t: [16]:

$$A(t_n) = \sum_i^N g(T_{2i})\,K(t_n, T_{2i}) + \varepsilon_n \quad (4)$$

where εn is an experimental noise, n is data points acquired over the time interval t.

Realization of the ILT procedure based on NNLS optimization yields a quasi-continuous distribution of amplitudes $g(T_2)$ from the dataset A(t). The NNLS optimization provides stability in the T_2 distribution curves obtained by ILT. It should be noted that we have compared the results obtained from the NNLS realization of the Prospa program with those from other versions of the ILT technique. Our investigations clearly indicate that the NNLS routine in PROSPA software yields the most stable results [17].

2.5. Testing the TD NMR Technique and the ILT Routine with $CuSO_4$ Aqueous Solutions

Prior to the TD NMR measurements of the sludge samples, we tested the performance of the relaxometry measurements and post-processing analyses of the relaxation curves using the Inverse Laplace Transform (ILT) by controllably varying the distribution of T_2 relaxation times in the reference samples. It is well known that the presence of paramagnetic ions in solutions shortens the T_2 relaxation times. In our case, we use $CuSO_4$ aqueous solutions to introduce paramagnetic Cu^{2+} ions, thereby reducing the relaxation time of water molecules [5]. Paramagnetic species introduce local magnetic field inhomogeneities due to their unpaired electron spins, thereby enhancing dipole-dipole interactions with the surrounding hydrogen nuclei in water molecules. These interactions accelerate the dephasing of transverse magnetization, thereby reducing the observed T_2 relaxation times. Consequently, higher $CuSO_4$ concentrations increase the density of paramagnetic centers, leading to stronger proton–electron interactions and faster relaxation [3]. In our case, CuSO4 solutions of varying concentrations (0.5 g, 1 g, 2 g, 3 g, 4 g, 5 g, and 6 g) were prepared and subsequently analyzed using TD-NMR relaxometry.

The T_2 values for each solution were determined by applying exponential fitting to the relaxation decay curves. Figure 2 presents the experimental spin-spin relaxation curves for the $CuSO_4$ solutions and the theoretical single exponential fits. The T_2 relaxation values obtained for these fits are given in the figure legend. Each experimental curve represents the average of five independent measurements performed for each sample, ensuring reproducibility and statistical reliability of the results.

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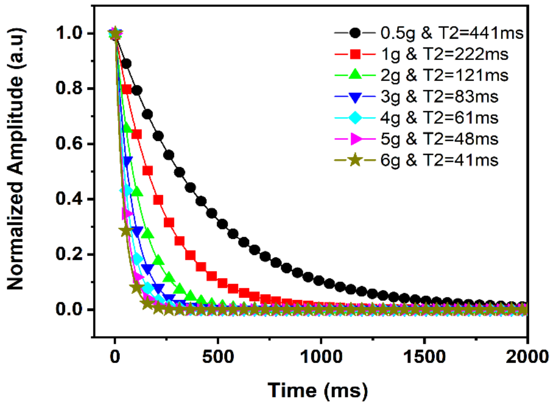

Figure 2. The observed NMR measurement signals from the $CuSO_4$ solutions.

The same relaxation curves were analyzed by the ILT-NNLS routine of the Magritek KEA software (Prospa), which provided the distribution of spin-spin (T_2) relaxation times for the $CuSO_4$ aqueous solutions (Figure 3). The relaxation distributions obtained by ILT show single Gaussian peaks with maxima exactly corresponding to the relaxation-time values from single-exponential fits.

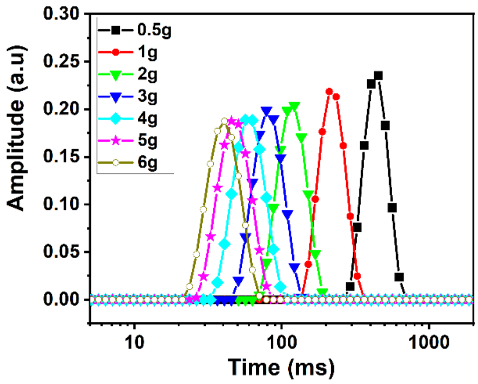

Figure 3. ILT distribution curves of different $CuSO_4$ samples.

Thus, we have demonstrated a robust operation of the ILT - NNLS routine for the case of controllable variation of T_2 relaxation times of water solution by addition of paramagnetic ions. The values of relaxation rates ($1/T_2$) versus $CuSO_4$ mass concentration are plotted in Figure 4.

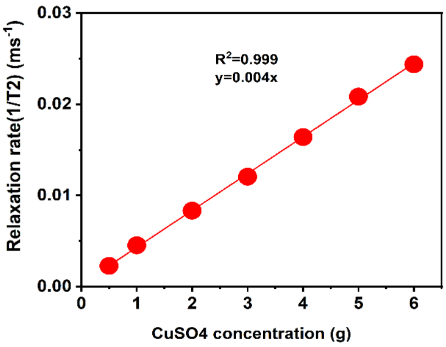

Figure 4. Dependence of T_2 relaxation rates on $CuSO_4$ concentration.

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The dependence of relaxation rates on the $CuSO_4$ mass matches perfectly with a linear fit with the coefficient of determination R^2 = 0.999, as expected from the literature. The relationship is described by Eq. 5:

$$y=0.004x \quad (5)$$

where y denotes the relaxation rate and x corresponds to the $CuSO_4$ mass [3,5,18].

3. Results

3.1. Arbitrary Areas of Various ILT Peaks for Three Groups of Sludge Samples

As described previously, the sludge samples were grouped into three categories. The first group represented inefficient dewatering, the second group represented relatively efficient on-site dewatering, and the third group corresponded to the highest dewatering performance, comprising samples subjected to additional laboratory centrifugation. Differences in the proportions of free and mechanically removable water were expected among these groups, with the highest proportion of free water anticipated in the first group and the lowest in the third. It was expected that the results of the ILT measurements would provide a quantitative measure of different water fractions in sludge samples. According to the literature, the first ILT peak corresponds to chemically bound water, the second to mechanically bound water, and the third to free water. To calculate the fraction of each water state, the area under each peak was integrated. The representative ILT curves for a selected sludge sample, successively processed to belong to each of the three groups described above, are shown in Figure 5. The arbitrary average areas under each peak for the three groups of samples in the first part of Table 3, while the arbitrary peak areas for the selected sludge sample processed to belong to all three groups are given in the second part of Table 3.

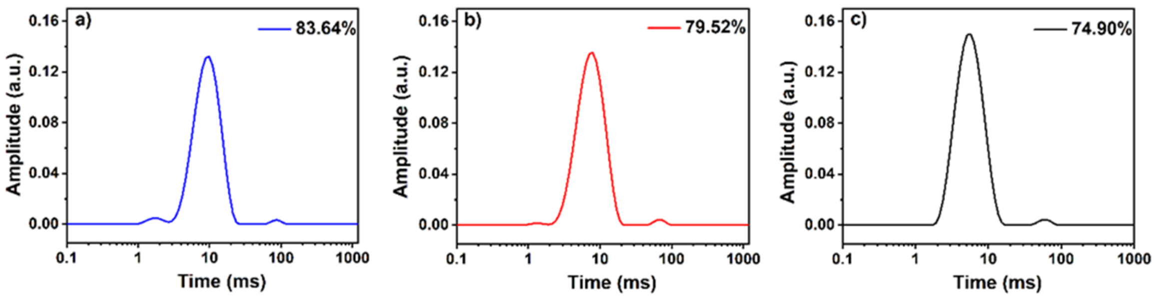


Figure 5. ILT of a selected sample for comparison.

Table 3. Area under the peaks of the ILT distributions corresponding to various water fractions.

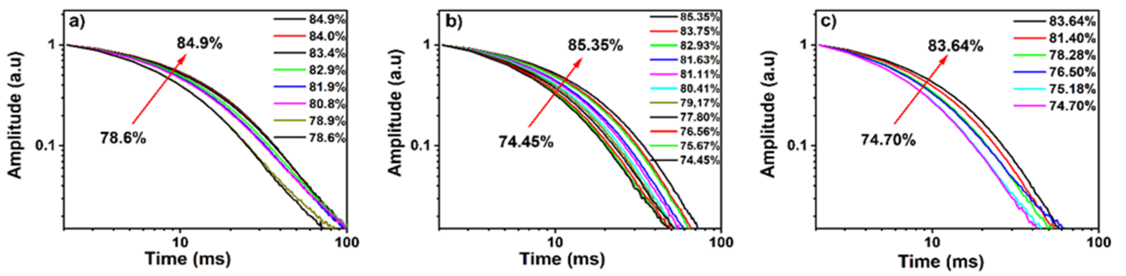
Sample characteristics	Moisture, %	Area under the 1st peak (chemically bound water), %	Area under the 2nd peak (mechanically bound water), %	Area under the 3rd peak (free water), %
Average of all sludge samples				
Samples representing inefficient dewatering	83.1	0.21	87.7	12.1
Samples representing efficient dewatering on-site	79.2	0.002	87.198	12.8

Samples representing the highest dewatering performance	75.4	-	89.9	10.1
Different states of a *selected* sludge sample for comparison				
Inefficient dewatering	83.6	0.33	93.3	6.4
Efficient dewatering (on-site)	79.5	0.02	91.1	8.9
Further centrifuged in the lab	74.9	-	88.6	11.4

Comparing various sample groups, we see no clear trend in the arbitrary ratios of the chemically bound, mechanically bound, and free-water ILT peaks (the first part of Table 2). It is expected that dewatering will decrease the ratio of free water to other fractions. We observe a slight decrease in the average free-water ILT peak ratio, but only in the third group (water content between 74.4% and 76.6%). On the other hand, as demonstrated in the second part of the table ("Different states of a selected sludge sample for comparison"), the proportion of mechanically bound water decreased as expected with increasing dewatering efficiency, while the free water ILT peak did not follow the anticipated trend. The ILT peak related to chemically bound water is not expected to be affected by dewatering performance. Unfortunately, due to the very low amplitude of this peak, it is difficult to trace reliably. varied among the sludge sample groups. In this respect, the work of Sun et al. (2025), in which the distribution of water fractions was re-analyzed, is remarkable. In this work, it was shown that the TD-NMR measurements with the following ILT are a qualitative tool rather than an exact quantitative measure of various water fractions in sludges. Our investigation also demonstrates that the areas under the ILT T_2 distribution curves cannot be used directly to quantify water-fraction distributions in waste sludge samples, consistent with the findings reported by Sun et al. (2023, 2025).

3.2. TD-NMR Measurement Results for Various Sets of Sludge Samples

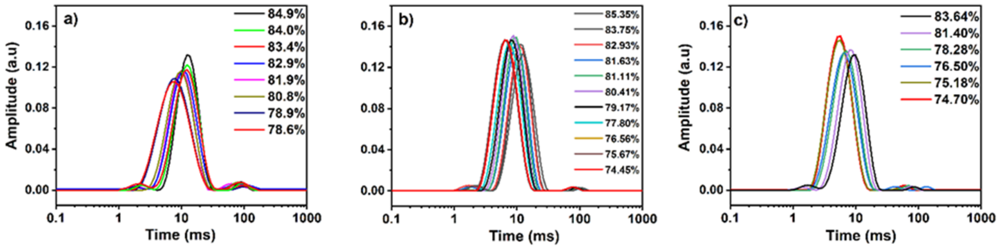
TD-NMR measurements were conducted on 26 sludge samples with water contents ranging from about 74% to 85%. Three different sets of samples, collected at various times, have been analyzed. (Each set of samples spans all three groups, discussed in the section above.) They are referred to as sets 1, 2, and 3 in the figures. The corresponding spin-spin (T_2) relaxation curves for all sample sets are presented in Figure 6.



(a) (b) (c)

Figure 6. The observed NMR measurement signals from the sludge samples in log-log scale (**a**: Set 1; **b**: Set 2; **c**: Set 3).

To assess the potential influence of noise on the distributions of the T_2 relaxation constant obtained by the Inverse Laplace Transform (ILT), measurements with different numbers (1, 4, and 36) of scans (repetitions) of the CPMG sequence for noise averaging were performed for the selected samples. These tests reveal that even a single-scan CPMG signal is adequate to receive a stable ILT distribution. T_2 distribution curves for all three sets of the sludge samples with varying moisture contents are presented in Figure 7. The relaxation time distribution profiles derived from our measurements show a clear resemblance to those reported in earlier studies [4,14,20].



(a) (b) (c)

Figure 7. ILT distributions of the T_2 relaxation time for sludge samples with varying water contents (a: Set 1; b: Set 2; c: Set 3).

The moisture content in the sludge directly correlates with the T_2 relaxation profile recorded by TD-NMR instruments. The transverse relaxation time (T_2) characterizes the mobility and binding environments of the hydrogen protons. As the moisture content of the samples increases, the T_2 values shift to the right, indicating a slowdown in spin relaxation dynamics in correspondence with the literature [4,14]. More water leads to less confinement, increasing water-molecule mobility and enhancing the averaging effect. ILT analysis of the sludge sample generally reveals three distinct peaks [5,8,21] attributed to different states of water: 1. The first peak (bound water), occurring at short T_2 relaxation times (T_2 = 1.7-2.4 ms), is indicative of water that is tightly attached to the solid particles , and to macromolecular surfaces. 2. The second peak (mechanically bound water) is in the range of intermediate T_2 relaxation times (T_2 = 7-20 ms), and corresponds to water that is mechanically associated/entrapped within the solid matrix, or is weakly interacting with the solid phase. 3. The last peak (free water) that appears at long T_2 relaxation times (T_2 = 63-120 ms) is indicative of nearly unbounded water that is free to move. This free water is mostly found in the void spaces of the material. When water content drops below ~80%, for some of the samples, the first peak vanishes, likely due to overlap between two peaks: tightly bound water and mechanically restricted (capillary) water. In accordance with the literature, in the studied water content region (70 – 90%), the ILT area of the mechanically bound water is much higher than that of other water types [3–5].

3.3. Correlation Between Water Content and TD-NMR Data

Based on the ILT distributions of the T_2 relaxation time for sludge samples (Figure 7), correlations between the absolute value of the integral area under ILT peaks and water content have been studied. We found that water content correlated with both the T_2 relaxation time of the 2nd peak (mechanically bound water) and the absolute value of the integral area under all ILT peaks. The correlation curve between moisture content and T_2 relaxation times for the 2nd peak (Figure 8a) is exponential and similar across all three sets of sludge samples. This means that variations in mineral or organic content and particle dispersion size, which are natural across three sets collected at different times, have little effect on the relaxation times of samples with similar water content. On the other hand, the area under the ILT relaxation curve peak and the water content reveal a linear correlation within a selected set (see Figure 8b).

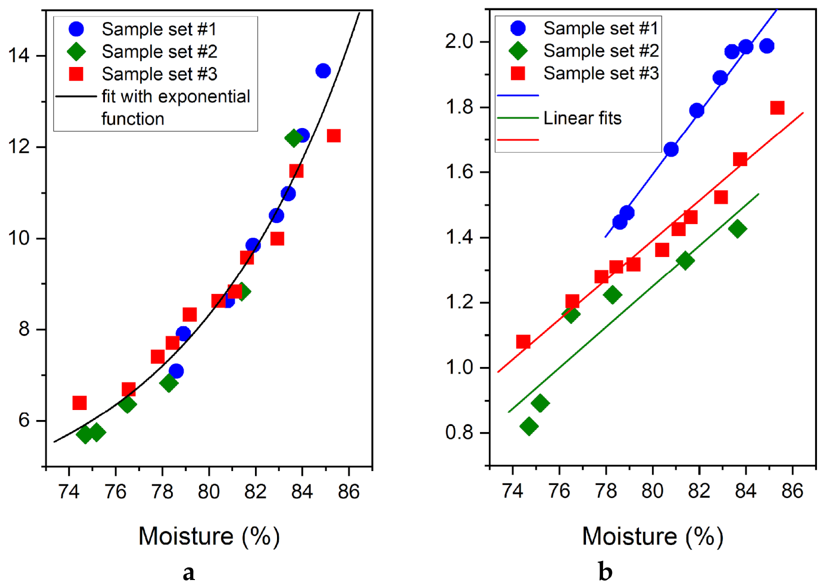


Figure 8. (a) – Dependence of the T_2 relaxation time of the second peak in the ILT distribution on the water content for three different sets of the sludge samples. The solid line represents the fit with an exponential function. (b) Dependence of the total area under all three peaks in ILT distribution on the water content for three different sets of the sludge samples. The solid lines represent the linear fits to each set of samples.

For comparison, an analysis based on least-mean-square fitting to the experimental data using a discrete set of exponential decays has also been applied. Three discrete exponents, each with different coefficients and relaxation times, have been used to model the relaxation curves of sludge samples. The dependences of the T_2 relaxation time of the second component on the moisture for three different sets of the sludge samples are given in Figure 9a. The dashed line represents the exponential fit for the second (largest) set of samples. (b) Dependences of the intensities of all three components in the three-exponential fittings for different sets of the sludge samples are given in Figure 9b. The dashed lines represent the linear fits to each set of samples.

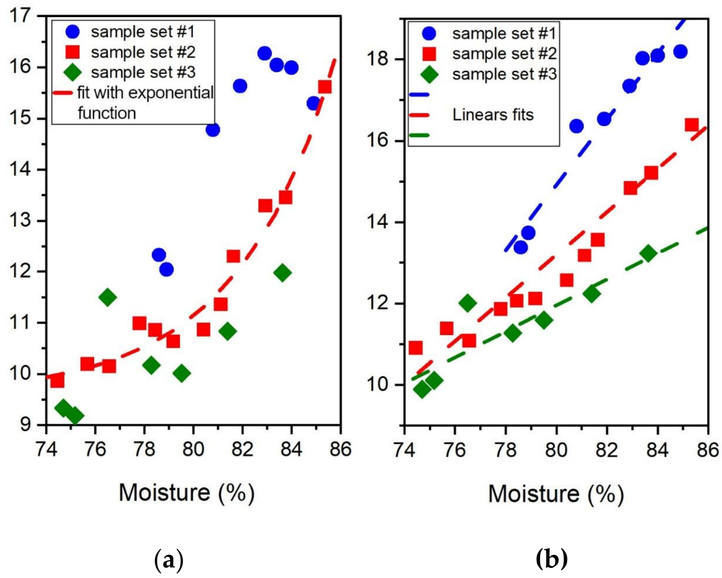


Figure 9. (a) – Dependence of the T_2 relaxation time of the second component on the moisture obtained by fitting with three discrete exponents. Three different sets of the sludge samples are given. The dashed line represents the exponential fit. (b) Dependence of the intensities of all three components for fitting with three discrete exponents. Three different sets of the sludge samples are given. The dashed lines represent the linear fits to each set of samples.

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A remarkable difference between the dependencies shown in Figures 8a and 9a is evident. The exponential correlation curve between water content and T_2 relaxation times for the 2nd peak is similar across all three sets of sludge samples in the ILT analysis (Figure 8a), whereas it exhibits significant dispersion in the discrete exponent set (Figure 9a).

The closer agreement of the second-peak T_2 values obtained by ILT across different sample sets is related to the fact that ILT represents sludge as a continuous distribution of relaxation environments, whereas the discrete three-exponential model forces the heterogeneous decay into only three effective compartments. However, sludge is inherently a complex system that is naturally expected to exhibit a continuous distribution of relaxation environments and obviously cannot be represented as three perfectly discrete populations [5,8]. In such systems, the ILT method is better suited to represent the measured CPMG decay because it resolves a distribution of T_2 components instead of forcing the signal into a limited number of mono-exponential terms. As a result, the second ILT peak more naturally reflects the center of the dominant intermediate-mobility water population, which remains comparatively stable between sample sets even when the peak width or amplitude changes. By contrast, the discrete three-exponential model imposes an oversimplified description of the decay, so the fitted middle component becomes an effective compromise parameter whose T_2 value depends not only on the intermediate water itself but also on how the adjacent shorter- and longer-T_2 contributions are partitioned during fitting. This forces the second T_2 value in the discrete three-exponential fit to be more sensitive to sample-dependent redistribution of component intensities, whereas the second peak derived from ILT is more robust and therefore shows lower variability across different sets of sludge samples [21].

An exponential character of the correlation curve between the water content and T_2 peak relaxation time (Figure 8a) has already been observed in literature [19]. Apparently, this is because various water fractions cannot be characterized by fixed parameters. Instead, different states of water are interlinked rather than distinct.

As described previously, the sludge samples were grouped into three categories to evaluate the effectiveness of TD-NMR in distinguishing water fraction distributions. The first group represented inefficient dewatering, the second group represented relatively efficient onsite dewatering, and the third group corresponded to the highest dewatering performance, comprising samples subjected to additional laboratory centrifugation. Differences in the proportions of free and mechanically removable water were expected among these groups, with the highest fractions anticipated in the first group and the lowest in the third group.

The results of the water content distribution, based on the area under each peak representing different water fractions—where the first peak corresponds to chemically bound water, the second peak to mechanically bound water, and the third peak to free water—are summarized in Table 3. As shown in the table, the proportion of mechanically bound water decreased as expected with increasing dewatering efficiency. However, the other fractions did not follow the anticipated trends. The proportion of chemically bound water, which was not expected to be affected by dewatering performance, varied among the sludge sample groups. Furthermore, the proportion of free water, which was expected to decrease, instead increased, contrary to expectations. Previous studies have also reported contradictory results regarding the representativeness of TD-NMR for water fraction distribution. This systematic investigation demonstrates that TD-NMR was not effectively responsive for water fraction distributions in waste sludge samples, which is consistent with the findings reported by Sun et al. (2025) in the literature. This might be caused by the overlapping of smaller peaks by the dominant second peak.

4. Conclusion

In line with the literature, the arbitrary areas under the peaks of the ILT T_2 distribution did not directly provide a quantitative estimate of water fractions across the different sludge samples. However, this study indicates a strong correlation between sludge water content and key parameters of the T_2 distribution curves, including the peak relaxation times and the area of the main peak. The relaxation time of the second peak provides the clearest common descriptor across different sample sets, suggesting it may be particularly useful for comparative measurements or online water-content monitoring. The total area of the T2 distribution also correlates strongly with water content, but this parameter should preferably be used together with careful calibration for each sludge type or measurement batch. Thus, this study highlights the potential of TD-NMR as a reliable, rapid, and non-destructive method for estimating sludge water content, while also indicating that peak-position-based metrics may be more robust than absolute peak-area metrics when comparing measurements across different sample sets.

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