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^{1}H NMR RELAXOMETRY AND ATR-FT-IR SPECTROSOPY USED FOR THE ASSESMENT OF WASTEWATER TREATMENT IN SLAUGHTERHOUSE

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ABSTRACT. Advanced ^{1}H NMR relaxometry based on fast Laplace inversion analysis combined with ATR-FT-IR spectroscopy, pH, electric conductivity and TDS (total dissolved solids) measurements were used to assess the purification process for chicken slaughterhouse wastewater. The ^{1}H NMR T_2-distribution (able to separate the effect of dissolved pollutants from undissolved pollutants), various integrated areas of IR spectra, the behavior of pH, electric conductivity and TDS show an efficient purification treatment for chemically treated water and evacuated water.

Keywords: *^{1}H NMR relaxometry, T_2-distribution, ATR-FT-IR spectroscopy, wastewater monitoring, slaughterhouse.*

INTRODUCTION

Large volume of water (15 000 - 20000 L per 1000 birds) is consumed daily into a chicken slaughterhouse along the entire production line. Unfortunately, this water consumption leads to an intense poultry process,

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since the resulted water is loaded with organic matters and can no longer be returned to the environment, usually via effluents [1, 2]. Therefore, purification treatments of wastewater before evacuation are mandatary. Regular methods largely used to monitor the wastewater purification process are based on the global measurements of apparent color, turbidity, electric conductivity (EC), total suspended solids (TSS), total dissolved solids (TDS), pH, chemical oxygen demand (COD), and ammoniacal nitrogen (NH3-N).

The aim of this work is to implement and to use advanced methods like: i) ^{1}H NMR relaxometry combined with FLI (fast Laplace inversion) analysis and ii) ATR-FT-IR spectroscopy to assess the efficiency of the wastewater treatment process starting with the untreated water up to evacuated water passing through biologically and chemically treated water. The resulted sludge is also characterized. The main advantage of the use of ^{1}H NMR relaxometry method is the fact that by FLI analysis the distribution of microscopic parameters like transverse relaxation time (T_2) is obtained. This allows the discrimination between dissolved and undissolved solids (pollutants) which further can be differentiated by their degree of mobility. Finally, the results are compared with the classic measurements of pH, electric conductivity and total dissolved solids (TDS).

EXPERIMENTAL

The wastewater samples (untreated water, biologically treated water, chemically treated water, evacuated water and sludge) were collected from a chicken slaughterhouse from the north of the Transylvania, stored into 0.5 l plastic container, transported to Technical University of Cluj-Napoca and measured as soon as possible. Before each measurement the samples bottles were agitated to homogenize the content. We started with the measurement of the pH, electric conductivity and totally dissolved solids (TDS), then with ^{1}H NMR measurements and at the end we finish with the FT-IR spectroscopy. Between measurements the samples were stored in dark at room temperature.

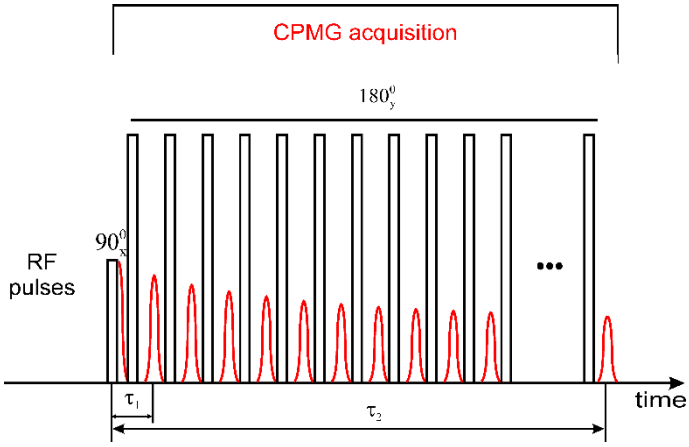

Fig. 1. The CPMG pulse sequence used for the [1]H NMR data acquisition.

The [1]H NMR relaxometry measurement of all wastewater samples was performed using a Bruker Minispec MQ 20 spectrometer (19.69 MHz working frequency) using the well knows CPMG pulse sequence (see Fig. 1) with echo time τ_1 = 5 ms. A number of 3000 echoes were registered. The recycle delay (RD) was set at 3 s and a number of 32 scans were acquired. The data were then processed using a fast Laplace-like inversion algorithm, intensively used in the last years to analyze multi-exponential decay curves [3-10].

The FT-IR spectra were recorded using a Jasco 6200 FT-IR spectrometer. For our liquid samples the ATR (attenuated total reflection) accessory was used and the ATR correction was performed for each spectrum. For background we use distilled water. The spectrometer set-up was as follow: i) the start wavenumber $\tilde{\nu}$ was 349.053 cm^{-1} but due to the noisy data at low wavenumber values the spectra were cutoff at 700 cm^{-1}; ii) the end $\tilde{\nu}$ was 4000.6 cm^{-1}; iii) to increase the signal to noise ratio (SNR) a number of 64 scans were accumulated; iv) the resolution was 4 cm^{-1}; v) a zero filling procedure was enabled and a cosine apodization procedure was performed; vi) the auto gain was set at 8, the auto aperture was 7.1 mm and the auto filter was 10 kHz; vii) the scanning speed was 2 mm/sec.

RESULTS AND DISCUSSION

The CPMG decay curves recorded for the slaughterhouse wastewater and sludge in the month 2 of monitoring are presented in Fig. 2a. One can observe a fast decay curve corresponding to biologically treated water indicating the presence of components with a reduced mobility. The slowest decay CPMG curve is obtained for the untreated water. A large superposition is observed between CPMG decays belonging to chemically treated water and evacuated water, suggesting that these samples have similarly properties. A slightly faster decay was obtained for the sludge resulted from wastewater treatment. As they are, these curves are hard to be further interpreted. A proper way of interpretation of the specific relaxometry data is via the analysis of the T_2-distribution obtained from CPMG decay, assumed to be multi-exponential [6-10].

The ^{1}H NMR T_2-distributions measured for the untreated water, the biologically and chemically treated water, the evacuated water and sludge resulted from treatment process are presented in Fig. 2b. The transverse relaxation

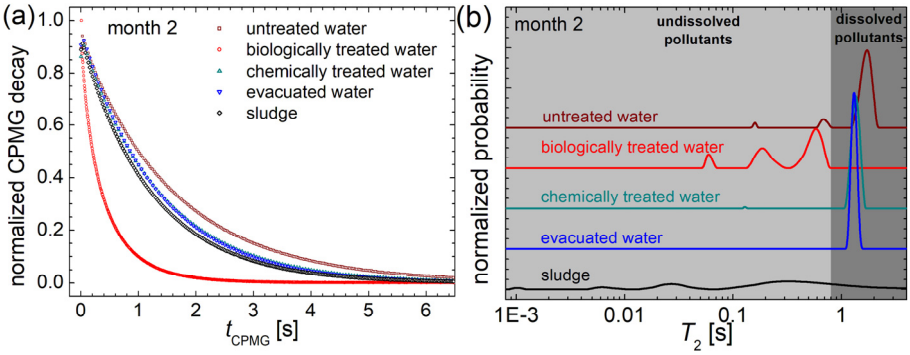

Fig. 2. (a) The ^{1}H NMR CPMG echo trains decays measured for the chicken slaughterhouse wastewater and sludge in the month 2 of monitoring; (b) The corresponding T_2-distributions.

times specific to wastewater were obtained in the range from ~ 50 ms up to 2.3 s. The untreated water and the biologically treated water are characterized by tree peaks, the chemically treated water is characterized by a main peak located at large T_2 values ($T_2 \cong 1.35$ s) and a very small peak located at small T_2

values ($T_2 \cong 128$ ms). The evacuated water is characterized by only one peak located at large T_2 values. With the exception of month 1 of monitoring, where for the untreated water and biologically treated water four peaks are observed, for the month three and four of monitoring only three peaks were also observed.

For the interpretation of these distributions the full T_2-distributions domain was spitted in two subdomains and associated, base on our experimental expertise on this subject, to: i) the domain of dissolved pollutants in water for T_2 values larger than 800 ms and ii) the domain of undissolved pollutants in water for T_2 values smaller than 800 ms. In our experimental set-up the distilled water is characterized by the most probable relaxation time T_2 value (at the peak maximum) of 2.4 s [4]. The dissolved solids with paramagnetic properties will lead to a decrease of this T_2 value. This decay is proportional with the content of dissolved solids but is also dependent on the pollutant nature. Nevertheless, one can say that a pure water is characterized by a large T_2 value.

The peaks that appear in the T_2-distributions in the domain of undissolved pollutants can be assigned to water molecules attached to solids of various sizes having then different mobility. Flotation and sedimentation processes of pollutants were observed at a simplest visual inspection. It is natural to associate the large T_2 value with more mobile water molecules hence with small undissolved pollutants. The medium mobile water molecules attached to medium size undissolved solids are characterized by peaks with T_2 values in the range of ~ 60 ms to ~ 170 ms. For month 1 of observation the T_2-distributions (not shown here) presents four peaks for untreated water and biologically treated water samples. There the fourth peak appearing to the smallest T_2 values (in the range of 45 – 47 ms) were associated with the less mobile water molecules attached to the largest pollutant particles.

In all 4 mounts of monitoring the T_2-distributions measured for the sludge are characterized by four peaks. These can be found in the range from ~ 0.9 ms up to ~ 515 ms. The peaks are more broaden compared to the peaks belonging to wastewater, regardless of the stage of treatment process, suggesting a more heterogeneous environment.

Further, in this paper the largest T_2 values characterizing the more mobile water pools (which may contain only dissolved pollutants) will be labeled as $T_{2,1}$ (see Fig. 3). The next peaks going from largest to smaller T_2 values (from right to left in Fig. 2b) are labeled, in order, with $T_{2,2}$, $T_{2,3}$, and $T_{2,4}$.

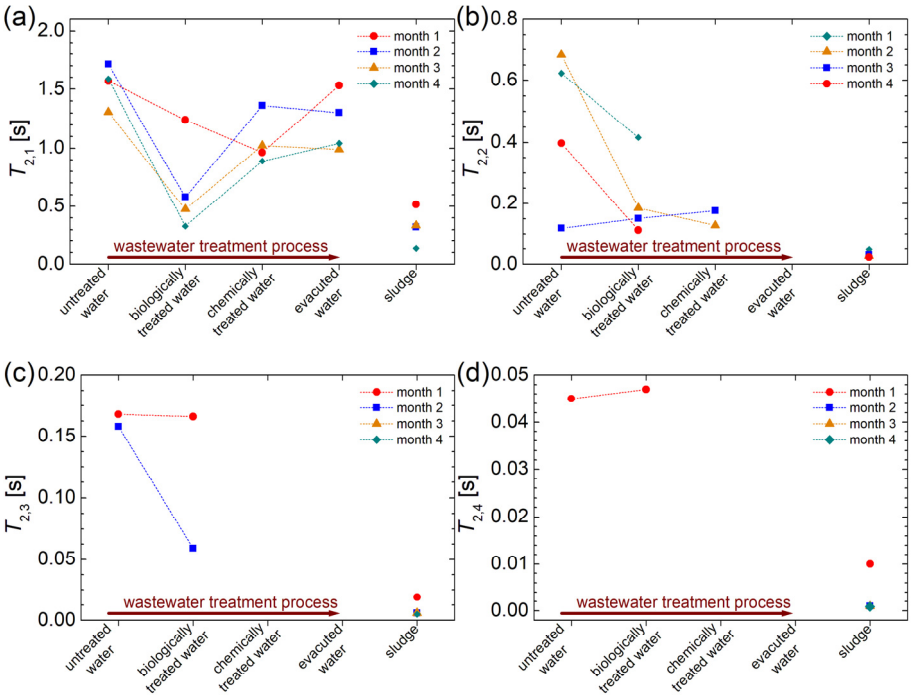

Fig. 3. The values of most probable transverse relaxation times associated to (a) dissolved pollutants ($T_{2,1}$); (b) most mobile water ($T_{2,2}$); (c) medium mobile water ($T_{2,3}$) and (d) water with restricted mobility ($T_{2,4}$) measured for the slaughterhouse wastewater (untreated water, biologically treated water, chemically treated water and evacuated water) and sludge for all four months of monitoring.

From the integral area under the peaks, which is proportional with the number of protons (^{1}H) mainly from each specific water pools, one can say that the untreated water is characterized (see Fig. 2b) by: i) a large amount of water with dissolved pollutants; ii) some undissolved pollutants with small dimensions and large mobility and iii) a small number of undissolved pollutants with medium size/mobility. As a result of biologically treatment

the peak characterized by the largest T_2 value ($T_{2,1}$) is found at the most lower values (see Fig. 3a) indicating that a large amount of pollutants were decomposed and dissolved in water. Other significant components of biologically treated water (see the relative area of peaks of the red distribution in Fig. 2b) are pollutants with reduced mobility of small and medium sizes (see the decay of $T_{2,2}$ in Fig. 3b and $T_{2,3}$ in Fig. 3c).

The efficiency of chemically purification treatment can be observed by the insignificant amount of proton signals associated with water molecules attached to the undissolved pollutants (see the dark cyan distribution in Fig. 2b). Such small amount of water with undissolved pollutants was measured in the months two and three of monitoring as can be seen from the existence of $T_{2,2}$ data in Fig. 3b. Also the increase of $T_{2,1}$ values for chemically treated water compared to those measured for biologically treated water indicates that the chemical treatment applied by the chicken slaughterhouse in this stage is efficient. The evacuated water in all four months of monitoring contain only a small amount of dissolved pollutants (see the $T_{2,1}$ values in Fig. 3a) while no water with undissolved pollutants was observed (lack of data for $T_{2,2}$ - $T_{2,4}$ in Figs. 3b to 3d).

In general all four T_2 values measured for sludge are smaller than the corresponding values measured for the wastewater (see Figs. 3). There is one exception where the $T_{2,1}$ values measured for sludge are comparable with those measured for biologically treated water. This is an indication of some similarities between the composition of water with dissolved pollutants from sludge and biologically treated water, which was also observed in the ATR-FT-ITR spectra. Such spectra were measured for samples obtained in months 2, 3 and 4 and are presented in Fig. 4.

At a visual inspection, the efficiency of the purification treatment process can be assessed from the overall spectral intensity. For the months 3 of monitoring the decay in the overall spectral intensity is not obvious. One can remark the relative decay of peak doublet located at ~ 2852 cm^{-1} and ~ 2920 cm^{-1} compared to the broad peak found between 2600 cm^{-1} and 3290 cm^{-1}. Contrary for the months 2 and 4 of monitoring the overall intensity of wastewater decay from untreated water (bottom spectra with wine color in

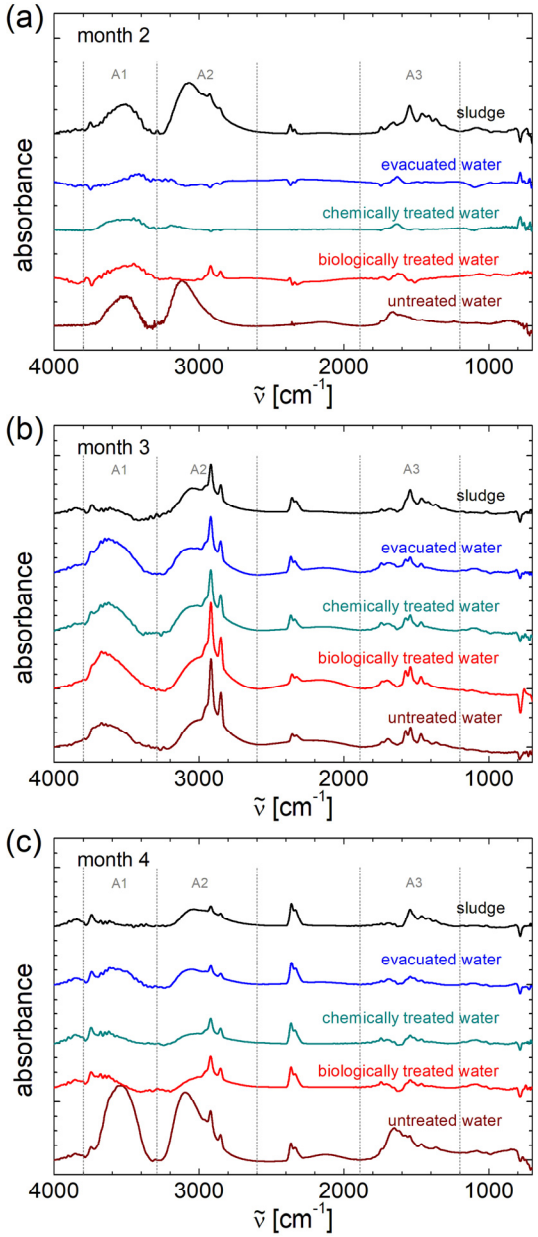

Fig. 4. The ATR-FT-IR spectra of measured for the slaughterhouse wastewater (untreated water, biologically treated water, chemically treated water, evacuated water) and sludge in the (a) second; (b) third and (c) forth month of monitoring.

Figs. 4) to evacuated water (spectra with blue line). As example, for the evacuated water sample obtained in month 2 one almost no absorption is observed. The sludge samples present similar features with the water samples since only the wet part could be measured.

The standard spectral analysis is hard to be interpreted since the pollutants are constituted from many types of organic matter. Therefore, the ATR-FT-IR spectra are divided in three specific regions as can be seen from Fig. 4 where light gray dashed lines delimitated the limits. The integral areas were calculated for these three domains as: i) A1 for the wavenumber domain from $\tilde{\nu}$ = 3290 cm^{-1} to $\tilde{\nu}$ = 3800 cm^{-1}, graphically represented in Fig. 5a; ii) A2 for $\tilde{\nu}$ = 2600 cm^{-1} to $\tilde{\nu}$ = 3290 cm^{-1}, graphically represented in Fig. 5b and iii) A3 for the wavenumber domain from $\tilde{\nu}$ = 1200 cm^{-1} to $\tilde{\nu}$ = 1890 cm^{-1}, graphically represented in Fig. 5c.

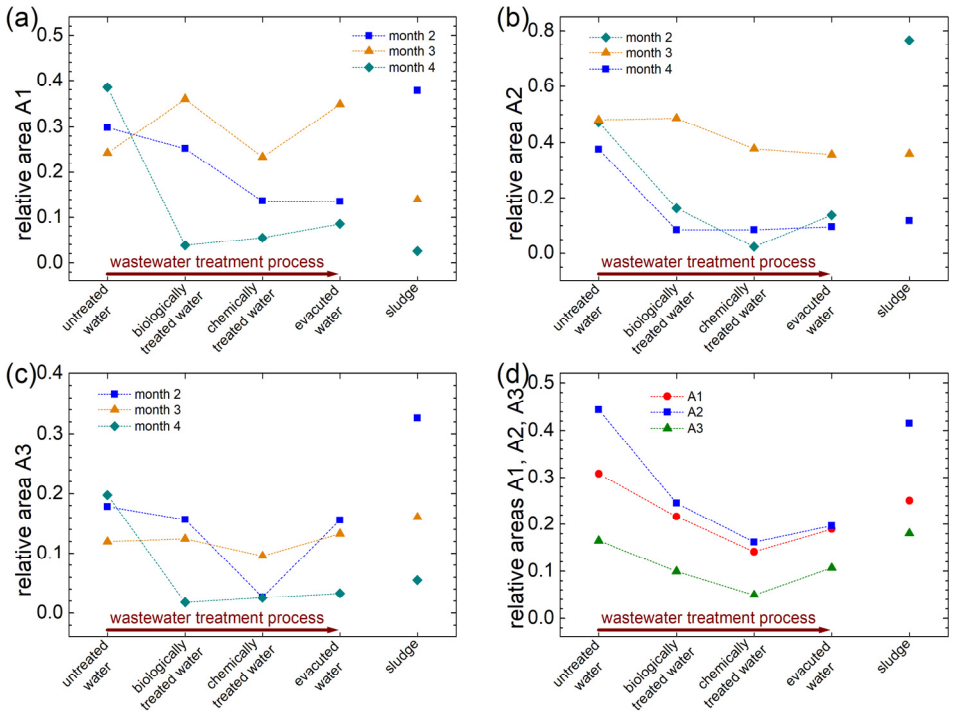

Fig. 5. The areas (a) A1; (b) A2 and (c) A3 as were defined for ATR-FT-IR spectra represented in Fig. 4 for the slaughterhouse wastewater and sludge.

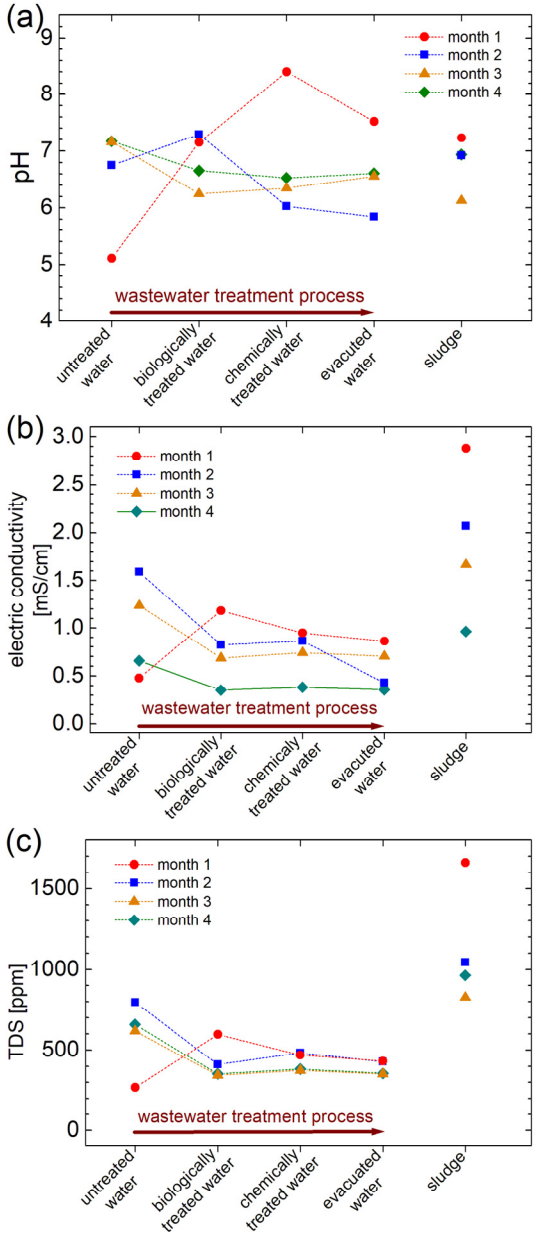

Fig. 6. The (a) ATR-FT-IR spectra of measured for the slaughterhouse wastewater (untreated water, biologically treated water, chemically treated water, evacuated water) and sludge in the (a) second; (b) third and (c) forth month of monitoring.

The average values of integrated areas A1, A2 and A3 over all three months are presented in Fig. 5d. Mainly the values of these integral areas calculated from absorbance spectra should reflect the concentration of pollutants but also the nature of pollutants may have a certain influence. All three parameters present a net decay from a higher value obtained for untreated water to biologically treated water and to chemically treated water. A slight increase of these areas can be observed for evacuated water. More increased values are obtained for sludge.

Selections of classic parameters were also measured and are graphically represented as follows: pH (Fig. 6a), electric conductivity (Fig. 6b) and TDS (Fig. 6c). With the exception of samples measured in the first months of monitoring for the reset of water samples one can observe an initial decay of pH, electric conductivity and TDS. Then, the values of these parameters, in the experimental error limit, will have similarly values. This is an indication of the fact that these parameters are not so sensitive.

CONCLUSIONS

The ^{1}H NMR T_2-distributions were used together with ATR-FT-IR spectra to evaluate the efficiency of the wastewater along the purification process (based on both biologically and chemically treatment) into a Transylvanian chicken slaughterhouse. We show that the advantage of using the T_2-distributions based analysis is the that one can discriminates between the water with dissolved solids from the water with undissolved solids and one can quantify the amount of pollutants in each reservoirs. By ^{1}H NMR relaxometry and IR spectroscopy it was shown that the quality of wastewater is significantly improved after chemical treatment. The measurement of classic parameters such as: pH, electric conductivity and TDS shown that they are not so sensitive, having similarly values for biologically and chemically treated water and for evacuated water, but in average indicating the water purification process.

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