Methods for biomass amount and sorption capacity estimation

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Abstract

Rising environmental standards for treated wastewater necessitate the improvement of current wastewater treatment methods or the need to look for new ones. Often this task is rather difficult because new or modified methods have to be investigated thoroughly and the main parameters for process modelling and effectiveness estimation have to be set. For instance, biomass concentration in the biosorption method is an important technological parameter although there is no accurate technique for its estimation. A thermal dissociation technique to determine biomass concentration was developed as an alternative to the standard volatile suspended solids (VSS) method.

Another important technological parameter in adsorption or biosorption processes is the sorption capacity of the sorbent. A simple technique was developed for the estimation of this parameter. The sorption capacity of the sorbent can be estimated using red formazane – a large-sized molecule compound–spirit solution. The results obtained show that this technique was quicker, simpler and more accurate than the standard procedure.

Keywords: biosorption, stable organic compounds, biomass, sorption capacity, technological control.

1 Introduction

One of the main technological parameters for the biological waste water treatment process control is the biomass amount variation during process time span. Biomass concentration is important for the technological calculations of the system, estimation of the oxidation potential and for the evaluation of biomass growth in accordance to decomposed pollutants, etc. Media of different types used in complex biological waste water treatment processes films over
with biomass and it becomes difficult to estimate biomass content and present it using identifiable units. The agglomerate media - biomass (active sludge) makes it impossible to use common method for the biomass estimation. The problem is that the biomass cannot be properly separated from the media. Also small particles of the media in the sample of active sludge would determine substantial analysis errors.

In the scientific literature usually methods for approximate biomass estimation can be found. The fluorescence of a fermentation culture was studied for its application as an estimator of biomass concentration [1]. But it is difficult to estimate biomass concentration in identifiable units, like g/l. Many factors have influence to exactitude of the analysis: temperature, pH, medium chemical composition and cell activity. Other authors [2] developed technique to determine biomass concentration as chemical oxygen demand (COD) as an alternative to the standard volatile suspended solid (VSS) method. But even using very small amounts of sorbent for COD analysis, COD values are very high. That is why this method can not be used for control of biosorption process. The modified micro-Kjeldahl and Lawry method [3] is designed for estimating amounts of organic nitrogen and proteins in the sample. These two components are the main components in the living cell, so it is possible to estimate biomass concentration from the results of this method. However, this technique has following limitations: (1) total organic nitrogen is measured, not only that in the cells; (2) the method requires careful standardization for any particular application; (3) the colour is not strictly proportional to the concentration. German scientists try to work out this problem. A very promising way appears to be the impedance spectroscopy which enables a fast determination of the biomass concentration even at high optical densities [4]. It utilizes the properties of the membranes of living cells which exhibit a high polarization and contribute a significant amount of capacitance to the impedance. The different polarization states of the cell yields a characteristic curve of permittivity from which the cell concentration can be derived. However this technology is in the initial stage yet and unique equipment is used. That is why another solution to solve this problem must be found.

Sorption capacity of the sorbent is another important parameter for technological control. Usually this analysis is performed using oil products. After the sorption period unabsorbed oil products are estimated according to ISO 9377- 2:2000 (E). However, quantitative determination of oil products is quite complicated, expensive, time consuming, analysis errors are determined by intermediates of biochemical petroleum degradation. Therefore it would be convenient to find another way to evaluate sorption capacity. We decided to use chromatic compound (red formazane) that would have molecular size close to the compounds of interest, fig. 1. In this way analysis would be less time consuming and more accurate.

This research covered two areas. The objective of our research was to develop and verify in practice accurate methodology for the determination of the biomass amount in the biosorption system, using fairly simple devices and to develop the technique for the estimation of sorption capacity of the sorbent.
The biomass amount and sorption capacity in AC (active carbon) and AS (active sludge) agglomerate – biologically activated system (BAS) – are the objects of this research.

![Molecular structure of red formazane.](image)

Biomass amount research tasks are: 1) to determine thermal dissociation dynamics for active carbon A in chosen temperature interval; 2) to determine thermal dissociation dynamics for active sludge in the same temperature interval; 3) to determine temperature points/interval, when the mass of both components is unvarying; 4) to verify methodology in practice.

Sorption capacity research tasks are: 1) to select stable chromatic organic compound; 2) to make its standard curve; 3) to carry out the experiments with chosen sorbent.

![Theoretical thermograms: 1) thermogram of AC; 2) thermogram of AS; 3) the temperature range acceptable for agglomerate heating.](image)

**2 Research methodologies**

**2.1 Biomass content estimation**

The equipment needed for the experiment is muffle furnace, analytical scale, ceramic melting pots, desiccator. AC sample is dried for 1 hour at temperature 105 °C until the stable mass. Then AC is heated at: 200, 300, 400, 500, 600, 700, 800 and 900 °C temperatures. As too big mass changes were observed in temperature intervals 300-400 and 400-500 °C, these intervals were divided into smaller intervals and the temperature sequence for experiments was chosen: 200, 300, 350, 400, 430, 460, 500, 600, 700, 800 and 900 °C.
At each temperature AC is heated till stable weight is reached. Preparation and analysis of AS is analogous to AC.

Theoretical thermograms of activated carbon and active sludge are represented in fig. 2. Their character was predicted before the experiment, i.e. it was premised that the curves would have three regions. These regions would represent temperature intervals when dissociation of both components does not take place, when dissociation takes place for both components and when both components are completely dissociated.

2.2 Sorption capacity estimation

The equipment needed for experiment is spirituous solution of red formazane, centrifuge with proper test tubes, photoelectrical colorimeter, tube shaker, transparent tubes, flasks of 50 ml and 250 ml.

\[
y = 0.0123x + 0.0362
\]

\[
R^2 = 0.9936
\]

![Figure 3: Calibration curve for red formazane spirituous solutions.](image)

2.2.1 Standardization (calibration) curve

Series of standard solutions are prepared. Red formazane concentration in these solutions is 50, 40, 30, 20, 10, 5 and 2 mg/l respectively. Optical density of the solutions is measured using photoelectrical colorimeter at wavelength 490 nm.

We obtained calibration curve with correlation coefficient \( R^2 = 0.9936 \), fig. 3. This means that the curve can be used for estimation of red formazane concentration in spirituous solutions without noticeable errors.

During the experiments sorption capacity was estimated for two biologically activated systems – BAS-A and BAS-B and for two active carbons A and B. Sorption capacity tests are performed for: active carbons A and B, at 105°C dried BAS-A and BAS-B, not dried BAS-A and BAS-B. For these tests samples are transferred into test tubes, then 5 ml of operating solution is added and tubes are shaken for 30 minutes. Solution is separated by centrifuging. Optical density is measured. Five replicates for each sample were analyzed.
3 Results and discussions

3.1 Biomass content research results

The characters of plotted experimental data were analogous with the character of theoretical curves, fig. 4.

![Experimental thermograms of AC-A and AS.](image)

Figure 4: Experimental thermograms of AC-A and AS.

The equation for the first region of curve of AC is:

\[
y_1 = 3 \times 10^{-7} t^2 - 0.0002t + 100
\]  

(1)

where \( y_1 \) – residual of activated carbon, %, in temperature range 100-400 °C; \( t \) – temperature, °C.

The correlation coefficient for this equation is \( R_1^2 = 0.98 \). The equation for the third region of curve of AS is:

\[
y_2 = 2 \times 10^{-6} t^2 - 0.0045t + 31.93
\]  

(2)

where \( y_2 \) – residual of active sludge, %, in temperature range 350-900 °C; \( t \) – temperature, °C.

The correlation coefficient for this equation is \( R_2^2 = 0.96 \).

The percentage weight loss at various temperatures for the same type of active carbon is similar. This allows to presume that ratios of samples weight between \( m_{350}^{AC} \) and \( m_{900}^{AC} \), \( m_{105}^{AC} \) and \( m_{900}^{AC} \) after heating at temperatures 105, 350 and 900 °C are constant. At the temperature 350 °C volatile organic part of active sludge almost completely dissociates and further rise of temperature has no effect on weight loss. Here we presume that ratio of residues weight after heating at 350 and 900 °C for the same type of active sludge is also similar. The results of these presumptions are the following formulas which enable to calculate organic part of biomass in the sample:
\[ m_{\text{org}} = m_{\text{AS}}^{105} - \alpha \cdot m_{\text{AS}}^{900} \]  

(3)

where \( m_{\text{org}} \) – organic part of biomass, g; \( m_{\text{AS}}^{105} \) - organic part of biomass in a sample after drying at 105 °C temperature, g; \( m_{\text{AS}}^{900} \) - residual of biomass (mineral part), after sample heating at 900 °C temperature, g; \( \alpha \) - constant.

\[ m_{\text{AS}}^{105} = m_{105} - D \times \frac{C \cdot m_{900} - m_{350}}{A - B \cdot C} \]  

(4)

\[ m_{\text{AS}}^{900} = \frac{m_{350}}{C} - \frac{B(C \cdot m_{900} - m_{350})}{C^2 (A - B \cdot C)} \]  

(5)

where \( m_{105}, m_{350}, m_{900} \) - sample weight after heating at temperatures 105, 350 and 900 °C, respectively, g; \( A, B, C, D \) – constants.

By means of eqn (1) and (2) under accepted presumptions constants \( A, C \) and \( \alpha \) can be calculated:

\[ m_{\text{AC}}^{105} / m_{\text{AC}}^{350} = \frac{3 \cdot 10^{-7} \cdot 105^2 - 0.0002 \cdot 105 + 100}{3 \cdot 10^{-7} \cdot 350^2 - 0.0002 \cdot 350 + 100} = 1.002 \approx 1 = \text{const.} A \]  

(6)

\[ m_{\text{AS}}^{350} / m_{\text{AS}}^{900} = \frac{2 \cdot 10^{-6} \cdot 350^2 - 0.0045 \cdot 350 + 31.93}{2 \cdot 10^{-6} \cdot 900^2 - 0.0045 \cdot 900 + 31.93} = 1.037 = \text{const.} C \]  

(7)

\[ \alpha = \frac{m_{\text{AS}}^{600}}{m_{\text{AS}}^{900}} = \frac{2 \cdot 10^{-6} \cdot 600^2 - 0.0045 \cdot 600 + 31.93}{2 \cdot 10^{-6} \cdot 900^2 - 0.0045 \cdot 900 + 31.93} = 1.015 = \text{const.} \]  

(8)

Constant \( B \) can be calculated using experimental data referring to presumptions mentioned above:

\[ m_{\text{AC}}^{105} / m_{\text{AC}}^{900} = 6.580 = \text{const.} B \]  

(9)

Equation for constant \( D \) is derived from eqn (4):

\[ D = \frac{A \cdot B}{C} \]  

(10)

It must be stressed that the values of all constants are the same only for the same type of active carbon and active sludge.

The temperature range for thermal separation of AS and AC composite (BAS) can be apparently seen in averaged values thermogram of active carbon and
active sludge, fig. 5. The first region of the curve (100-350°C) goes down because of dissociation of active sludge. The third region of the curve represents thermal dissociation of active carbon. The median horizontal region (350-400 °C) represents the range of temperature when the amounts of both components do not change, i.e. active sludge is dissociated already and thermal dissociation of active carbon has not begun yet.

![Figure 5: Averaged values thermogram of AC-A and AS.](image1)

3.2 Sorption capacity research results

The results from the experiments are shown in fig. 6. Two ACs and two BASs were tested during the research of sorption capacity: AC-A and AC-B, BAS-A and BAS-B. Sorption capacity of ACs samples was equated to 100%, fig. 6. (AC-A, AC-B). It was estimated that sorption capacity of AC-A and AC-B was 4.24*10^{-3} and 6.1*10^{-3} g/g of red formazane...
respectively. Initial sorption capacity of AC-B was 30.5% higher than that of AC-A. Test results of dried BAS-A and BAS-B samples show that sorption capacity of BAS-A sample stayed almost at the same level as the initial sorption capacity of AC-A. However sample BAS-B adsorption decreased 84%, fig. 6. (BAS-A (1), BAS-B (1)). During the experiment with not dried samples, sorption capacity of BAS-A increased 40%, according to initial sorption capacity. Sorption capacity of BAS-B makes only 30% of initial sorption capacity, fig. 6. (BAS-A (2), BAS-B (2)).

These results show that during the biosorption process BAS-A is regenerated by biomass. Sorbent BAS-B during the process is not regenerated, the stoppage of pores occurs and in the agglomerate of AS - AC only one active component – biomass stays and sorption characteristics of the system are lost.

4 Conclusions

1) It is experimentally proved that the heating process proceeds regularly. The relation between temperature and burnt out part of activated carbon at the temperature range 200-400 °C is strong and correlation coefficient is $R_1^2 = 0.98$. The relation between temperature and volatile organic part of active sludge at the temperature range 350 – 900 °C is strong and correlation coefficient is $R_2^2 = 0.96$.

2) The experimental research confirmed that organic volatile part of active sludge can be estimated after heating sample at the temperature of 350 °C. This value is used for calculating constants.

3) The ash content of the agglomerate active sludge - activated carbon is estimated at the temperature of 900 °C. This temperature is the final for heating samples.

4) Knowing weights of the samples after heating at the temperatures 105, 350 and 900 °C the organic part of biomass, the traditional (heated in 600°C) ash content of biomass and the mass of activated carbon in the sample can be estimated.

5) The modified technique for sorption capacity estimation is simple, quick and accurate.

6) Sorption capacity analysis with ACs results show higher sorption capacity of AC-B.

7) Examining biologically activated systems (carbon - alive biomass) much higher sorption capacity was observed for BAS-A than for BAS-B.

8) The method was verified on different BASs. It enables to evaluate the regeneration degree of sorption capacity of BAS.

References

