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Original Research

Estimation of Biomass Amount and Sorption Capacity for Technological Control of the Biosorption Process

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Abstract

The paper describes two modified methods to determine the main parameters of the biosorption system. One of them – biomass amount, is an important technological parameter that is needed for technological calculations of the equipment, for the evaluation of oxidation potential and biomass growth in accordance with decomposed pollutants, etc. Typically, VSS (volatile suspended solids) are used as a measure of microorganisms, but accurate evaluation of the organic part of biomass on the sorbent surface is complicated. Thermal investigation methods are based on different sorbent and biomass burning temperatures and the obtained results are suitable for biosorption process control.

Another important parameter is sorption capacity of the sorbent used in the process. The theoretical adsorption capacity of the activated carbon is usually estimated for a particular contaminant. The method, which in this case involves use of oil products, has been modified for the purpose of evaluation of this parameter. Quantitative analysis of oil products is quite complicated and time consuming. Therefore a colored and stable organic compound of large molecular size has been chosen. Concentration of this compound in spirit solution has been quickly and exactly estimated with a photoelectrocolorimeter.

Keywords: biosorption, amount of biomass, sorbent, sorption capacity, technological control

Introduction

Application of biosorption systems has started to meet the rising environmental standards for treated wastewater. The term "biosorption" is used here for a short description of the complex of granulated activated carbon and microorganisms (biologically activated system). Sorption, oxidation of pollutants and regeneration of the sorbent take place in such a system. Systems of granulated activated carbon are applied for removal of heavy metals from water [1]. They are distinguished for catalytic characteristics when ozonation removes organic carbon [2]. At the same time; biologically activated carbon has proven to be useful in removal of stable organic compounds of difficult biochemical disintegration [3, 4], as well as dyeing materials [5, 6, 7], gas [8] and volatile organic compounds [9] from wastewater. In these systems the sorbent serves as a basis for microorganism culture attachment and a means for concentration of the dissociated compounds. This complex system [10] is more stable and resistant to environmental changes and fluctuations of pollutants. However, due to complex technological control the biosorption systems are not widely spread and their investigation is limited to laboratory conditions. Dynamics of biomass variation in the course of technological wastewater treatment processes is one of the main control parameters that strongly influence efficiency of the process [11]. The problem arises due to the absence of proper estimation of biomass amount.

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The agglomerate sorbent – biomass (active sludge) makes it impossible to use the common method for the estimation of active sludge concentration. The reason is that the biofilm cannot be properly separated from the sorbent. Some biomass would remain in the pores of the sorbent. Also, small particles of the sorbent in the sample of active sludge would determine substantial analysis errors. Therefore, literature has been reviewed to find other methods of biomass amount determination that are also suitable for estimating biomass amount in biosorption systems.

The suggested modified method for estimation of biomass amount is one of the alternatives [12, 13]. In this method the amount of biomass is estimated by determining its COD value. Nevertheless, this method is not good for the biosorption process as even very small amounts of sorbent give high COD values, which strongly influence the precision of the analysis.

Zabriskie and Humphrey described the method of biomass amount estimation that is based on the fluorescence of cells [14]. Having lighted the medium with ultraviolet rays (366 nm), the nicotinamide-adenine-dinucleotide and nicotinamide-adenine-dinucleotide phosphate existing in cells fluorescate by radiating 460 nm length waves. However, a big number of factors influence the exactitude of the method: temperature, pH, chemical composition of the medium and biochemical activity of cells. This method does not solve the problem of solid admixtures. At the same time it is very complex and insufficiently accurate. Colorimeter and biocolorimeter methods of biomass estimation also require complex measuring equipment [15, 16].

A description of modified micro-Kjeldahl and Lawry method [17] for determining biomass is also found in scientific literature. This method joins the Kjeldahl and Lowry methods designed for estimating amounts of organic nitrogen and proteins in the sample. These two components are the main components in living cells, therefore determination of their amounts in the sample provides the possibility to calculate biomass amount. However, this technique has the following limitations: total organic nitrogen is measured, not only that in biomass; in the case of proteins' estimation the method requires careful standardization for any particular application; the colour is not strictly proportional to the concentration; incomplete and different degrees of reaction of sucrose, lipides, monosaccharides and hexosamines with the reagent has been proved; the analysis can be impeded by higher concentrations of ammonium sulphate, sulfohydrylic compounds and phosphates.

The estimation of biomass amount by means of ferment activity tests [18, 19] is not sufficiently accurate as a vital capacity of microorganisms is determined by many factors that seldom remain constant for a long time. Quantitative RNA evaluation can be used for exact estimation of live biomass [19]; however, this requires complex equipment.

German scientists are currently occupied with the problem of estimation of biomass amount. Muller supervises the project aimed at the creation and characterization of resistivity sensors [20]. So-called impedance spectroscopy enables determination of biomass amount in the samples containing high amounts of biomass and other suspended particles. The technology is based on the property of the membranes of living cells to polarize and to create certain resistivity. The obtained curves of permittivity, ε_r, enable us to derive the cell concentration. However, the impedance spectroscopy technology is still in the initial stage and uses unique equipment. Therefore, application of this method in research remains impossible and other ways to solve this problem must be found.

Sorption capacity of the sorbent is another important parameter for technological control. Usually sorption capacity of sorbents is analyzed by using oil products (ISO 9377- 2:2000 (E)). However, quantitative estimation of oil products is quite complicated, the analysis is time consuming, analysis errors are determined by intermediates of biochemical petroleum degradation. Therefore, having selected a colored compound that would have molecular size close to that of oil product compounds (Fig. 1) and using common means and equipment quick and accurate estimation of sorption capacity of sorbent is possible.

Two activated carbons were used in this research: A and B. Carbon A is made from anthracite, using special technology for its activation. Carbon B is coco-carbon, which is made using special technology for its activation.

The objective of this research was to develop the methodology that enables us to estimate biomass amount in the system of activated carbon by means of application of fairly simple and recognized devices. Also, the ability to use the methodology in practice was checked. This was done with different systems with known quantities of sorbent and known amounts of active sludge. Another objective was to adopt methodology for estimation of sorption capacity of activated carbon. This methodology is based on photocolorimetry.

The following tasks were set for estimation of biomass amount:

1. to determine thermal dissociation dynamics for activated 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/intervals, when the amounts of both components are unvarying;
4. to check the ability for practical use.

The object of this research was the amount of biomass in agglomerate active sludge-activated carbon (biologically activated system – BAS).

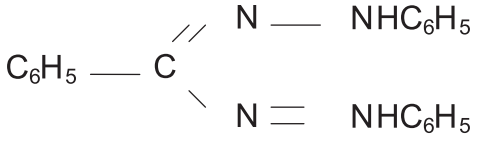

Fig. 1. Molecular structure of red formazane.

The following tasks were set for investigation of sorption capacity:

1. to select a stable chromatic organic compound;
2. to calibrate a graph of its concentration;
3. to use the chosen sorbent in the investigation of sorption capacity.

The object of this research was sorption capacity of the sorbent used in the biosorption process in active sludge-activated carbon agglomerate.

Methods

Biomass Amount Estimation

The equipment needed for the experimental estimation of biomass amount are a muffle furnace, ceramic melting pots and a desiccator.

Analytical scale is used to weigh 50 g of activated carbon, which is dried at 105^{0}C until stable mass. After that the carbon is heated at the following temperatures: 200, 300, 400, 500, 600, 700, 800 and 900^{0}C. The obtained data shows significant mass changes in the temperature intervals 300-400^{0}C and 400-500^{0}C. Therefore, these intervals are divided into smaller intervals and the following sequence of temperatures appears: 200, 300, 350, 400, 430, 460, 500, 600, 700, 800 and 900^{0}C.

At each temperature the carbon is kept until a stable weight is reached. After each heating the cooled off carbon is weighed and the burnt down part is calculated.

Samples of active sludge are prepared. They are dried at the temperature of 105^{0}C until stable mass and heated by using the same methods as that in the case of activated carbon samples.

Theoretical thermograms are shown in Fig. 2. Their character was predicted in advance, i.e. the curves were assumed to 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.

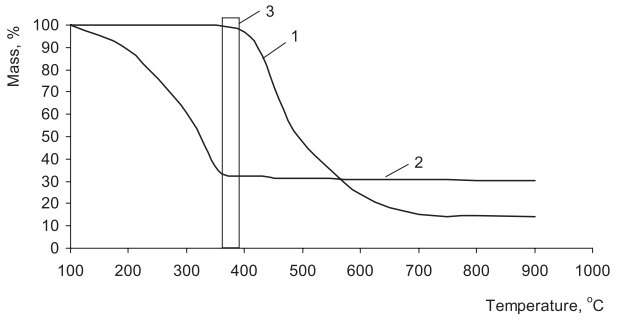

Fig. 2. Theoretical thermograms of activated carbon and active sludge. 1 – thermogram of activated carbon; 2 – thermogram of biomass; 3 – temperature interval for heating of samples.

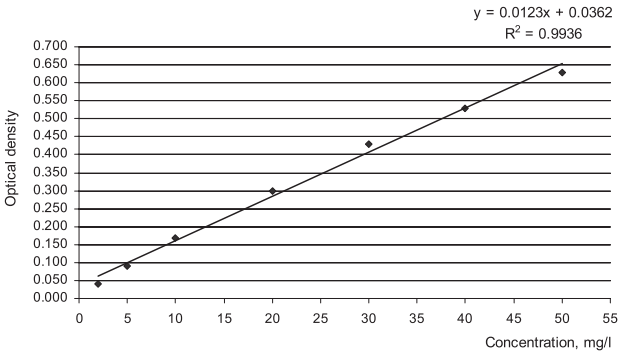

Fig. 3. Calibration curve of red formazane.

Sorption Capacity Estimation

The equipment and reagents used for sorption capacity investigation are as follows:

- spirituous solution of red formazane;
- centrifuge;
- centrifuge test tubes of 11ml useful volume
- photoelectrical colorimeter;
- tube shaker;
- 0,5 cm length cells;
- flask of 250 ml;
- flasks of 50 ml.

Calibration Curve

A calibration curve is developed by using operating solution of formazane.

A series of standard solutions is prepared, in which concentrations of red formazane per 1 l of ethyl spirit are 50, 40, 30, 20, 10, 5 and 2 mg. Optical density of the solutions is measured by using a photoelectrical colorimeter at wavelength of 490 nm (blue filter) and by using cells of 0.5 cm length. Calibration curve of the dependency of optical density of solutions on their concentration mg/l is drawn (Fig. 3). The curve is straightened. Correlation coefficient $R^2 = 0.9936$ shows strong relation between the obtained dependency and the straightened curve, and the possibility to use it for estimation of red formazane concentration mg/l according to optical density of the solution.

This method was used to determine sorption capacities of activated carbons A and B and of biologically activated systems (BAS). Red formazane operating solution of 50 mg/l concentration was prepared for the investigation of sorption capacity. Adsorption experiment was done under three different conditions: clean and dried activated carbons A and B, BAS-A and BAS-B, dried at 105^{0}C, and non-dried BAS-A and BAS-B. Then 5 ml of operating solution was added to all samples and the tubes were shaken for 30 minutes. After that the operating solution was poured and centrifuged at 4000 rotations/min and its optical density was measured with

photoelectrical colorimeter. The experiment was repeated five times.

Results and Discussion

Biomass Content Investigation

After the experiment the obtained data was plotted (Fig. 4).

The comparison shows that theoretical curves (Fig. 2) and those developed during the experiments are analogous. The obtained results are used to deduce formulae for calculation of biomass content.

The equation that describes the first region of activated carbon curve was selected:

$$y_1 = 3\cdot10^{-7}\, t^2 - 0.0002\, t + 100 \qquad (1)$$

where:
y_1 - residual of activated carbon % in the temperature interval 100-400^{0}C, t - temperature, ^{0}C.

The correlation coefficient of this equation is R_1^2=0.98.

The following equation describes the third region of active sludge curve:

$$y_2 = 2\cdot10^{-6}\, t^2 - 0.0045\, t + 31.93 \qquad (2)$$

where:
y_2 - residual of active sludge % in the temperature interval 350-900^{0}C, t - temperature ^{0}C.

The correlation coefficient of this equation is R_2^2=0.96.

The percentage weight loss at each temperature for activated carbon A and biomass has been determined on the basis of five repetitions. The difference of obtained meanings is ± 5%. This allows for the presumption that the weigh ratio of carbon A after heating at different temperatures is reliable and constant. A similar situation is reported in the case of active sludge. This results in formulae that enable us to calculate organic part of biomass in the sample.

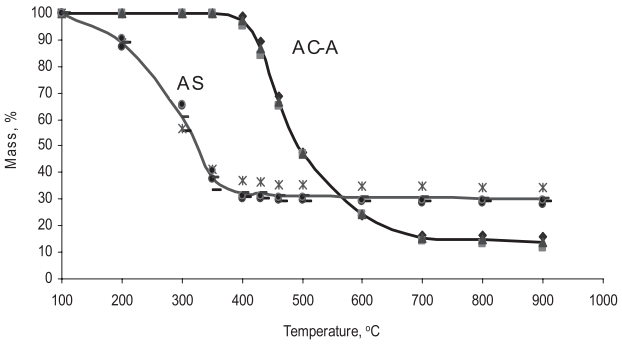

Fig. 4. Experimental thermograms of active sludge and activated carbon A.

$$m_{org} = m_{105}^{AS} - C\cdot m_{900}^{AS} \qquad (3)$$

where:
m_{org} - organic part of biomass, g
m_{105}^{AS} - part of biomass in the mixture, dried at 105^{0}C, g
m_{900}^{AS} - residual of biomass (mineral part), having heated the mixture at 900^{0}C, g
C - constant

$$m_{105}^{AS} = m_{105} - E\times\frac{B\cdot m_{900} - m_{350}}{A - D\cdot B} \qquad (4)$$

$$m_{900}^{AD} = \frac{m_{350}}{B} - \frac{D(B\cdot m_{900} - m_{350})}{B^2(A - D\cdot B)} \qquad (5)$$

where:
m_{105}, m_{350}, m_{900} - sample weight after heating at the temperatures of 105, 350 and 900 ^{0}C, respectively, g.
A, B, D, E - constants

Following the accepted presumptions equations (1) and (2) can be used to calculate the constants A, B and C:

$$m_{105}^{AC}/m_{350}^{AC} = \frac{3\cdot10^{-7}\cdot105^2 - 0.0002\cdot105 + 100}{3\cdot10^{-7}\cdot350^2 - 0.0002\cdot350 + 100} = 1.002 \approx 1 = const.A \qquad (6)$$

$$m_{350}^{AS}/m_{900}^{AS} = \frac{2\cdot10^{-6}\cdot350^2 - 0.0045\cdot350 + 31.93}{2\cdot10^{-6}\cdot900^2 - 0.0045\cdot900 + 31.93} = 1.037 = const.B \qquad (7)$$

$$m_{600}^{AS}/m_{900}^{AS} = \frac{2\cdot10^{-6}\cdot600^2 - 0.0045\cdot600 + 31.93}{2\cdot10^{-6}\cdot900^2 - 0.0045\cdot900 + 31.93} = 1.015 = const.C \qquad (8)$$

Constant D can be calculated using experimental data and following the presumptions mentioned above:

$$m_{105}^{AC}/m_{900}^{AC} = 6.580 = const.D \qquad (9)$$

Constant E is obtained by deriving the equation (4):

$$E = \frac{A\cdot D}{B} \qquad (10)$$

It should be indicated that these constants have similar values only for the same type of active sludge and activated carbon.

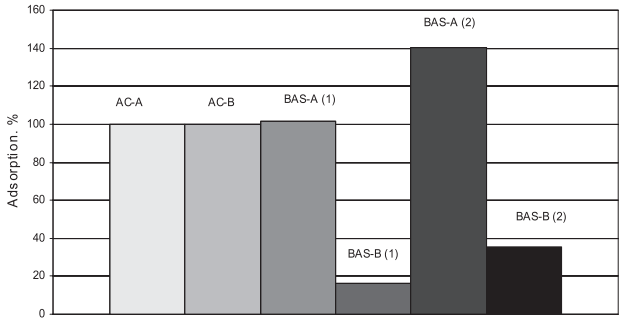

Fig. 5. Results of sorption capacity investigation.

Sorption Capacity Investigation

Graphical image of the results, received during the experiment, is shown in Fig. 5.

Two biologically activated carbons BAS-A and BAS-B were used for the investigations. Weights of the samples were 0.05 g. Sorption capacity of clean, uncovered with biomass and unused samples of activated carbon equaled 100% (AC-A and AC-B). The experiments established sorption capacity of AC-A to be $4.24*10^{-3}$ g/g of red formazane, and that of AC-B – $6.1*10^{-3}$ g/g. Initial sorption capacity of AC-B was 30.5% higher than that of AC-A. Results of biomass covered and dried samples investigation showed that sorption capacity of BAS-A samples stayed almost at the same level as the initial sorption capacity, while that of BAS-B decreased more than five times (BAS-A (1) and BAS-B (1)). During the experiment with the samples that had not been thermally treated, i.e. live biomass on the sorbent, sorption capacity of BAS-A samples increased by two fifths in comparison with initial sorption capacity of clean sorbent. At the same time sorption capacity of BAS-B made only one third of initial sorption capacity (BAS-A (2) and BAS-B (2)). These results show that during the biosorption process activated carbon A was regenerated by the film of microorganisms. During the process sorbent B was not regenerated, the stoppage of pores occurred and only one component – biomass – remained effective in the agglomerate of microorganisms and sorbent, while sorption charasteristics were lost.

Conclusions

1. The experiments have confirmed that ashless mass of active sludge can be estimated by heating the sample at 350^0C, the value of which is used for calculating constants.
2. The final heating temperature is 900^0C; at this temperature ash content of the mixture of activated carbon and active sludge is estimated.
3. Availability of total weights of the samples, heated at 105, 350 and 900^0C, makes it possible to calculate the organic part of biomass in the sample, ash content in the biomass at 600^0C and mass of activated carbon.
4. Examining the samples of clean sorbents distinguished sorbent B for higher sorption capacity.
5. Examining the samples of the sorbents, covered with live biomass (not dried sample), showed significantly higher sorption capacity of BAS-A.
6. During the process sorbent A is able to regenerate, to renew its sorption capacity, while sorbent B loses this property, the stoppage of sorbent pores occurs and only one part of the complex – biomass – remains effective and useful for the process.
7. BAS-A is suitable for the biosorption process due to remaining sorption capacity, its biochemical regeneration and development of the basis for microorganisms' attachment.

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