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Impact of the excess sludge modification with selected chemical reagents on the increase of dissolved organic substances concentration compounds transformations in activated sludge

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ABSTRACT

Submission of excess sludge initial disintegration process significantly affects the efficiency of anaerobic stabilization process. Expression of increasing the concentration of organic matter in dissolved form is to increase sludge disintegration. As a result of chemical modification is an increase of the chemical oxygen demand and the concentration of volatile fatty acids. The aim of this study was to determine the impact of the disintegration process with selected chemical reagents to increase the concentration of organic substances in dissolved form. The process of chemical disintegration of excess sludge was treated using the following reagents: $Mg(OH)_2$, $Ca(OH)_2$, HCl, H_2SO_4, H_2O_2. The modification was carried out at ambient temperature for 2, 6 and 24 h. During sludge disintegration it was noticed the growth of indicators values that confirmed the susceptibility of prepared sludge to biodegradation.

1. Introduction

The main aim of wastewater treatment is protection of the purity of surface water and the human environment. The process of sewage treatment is always accompanied by the formation of sludge. They are defined as organic - mineral phase separated from the wastewater. The amount of sludge that is formed in the wastewater treatment plants depending on the composition of the wastewater, the degree and the way of their treatment, the biodegradability of sewage sludge and the degree of dehydration (Bień, 2011; Jabłonska and Siedlecka, 2015). In addition, an effective method of assessment of the structure and biological composition of sludge are, enjoying every time more interest, Non-Destructive Techniques (NDT) Analysis for example magnetic particle testing, ultrasonic or radiographic testing (Manikandan et al., 2011; Manikandan and Rajamannan, 2006; Ravisankar et al., 2005, 2007, 2006).

Excess sludge characteristic and properties may vary depending on the process, especially since a process for removing phosphorus and nitrogen compounds, the age of the sludge, due to the existence of pre-settling tank or lack thereof, which affects the amount of slurry transferred to activated sludge chambers. Too long stay excess sludge under anaerobic conditions have a negative impact on thickening and drainage (Malej, 2000). The excess sludge consists of a suspension of micro-organisms living and dead, and mold spore. Excess sludge is characterized by a high hydration (99 − 98%) and a high content of organic matter (75 − 65%). The use of disintegration shortens the process time anaerobic stabilization, speeding up the process of hydrolysis through the transfer of the organic load of the solid sludge phase dissolved. The result of the disintegration is the increase in the degree of fermentation sludge and intensification of biogas production (Grübel et al., 2013).

Disintegration of sewage sludge is a dynamically developing technology that determines the efficiency of the process of anaerobic stabilization. It is the process of introducing external energy to the sludge to break up the solid particles sludge and the processes of a lysis introduced. The destruction of the structure of sludge by external forces affect the release of intracellular components, determining a faster and more intense stabilization (Wolski and Malkowski, 2014a, 2014b; Zawieja, 2016). The effectiveness of a chemical disintegration directly depends on the type of reagent, its dose and exposure time of sludge (Watcharapol and Boonchai, 2014). Chemical disintegration can be carried out by the neutralizing processes i.e. acidic or alkaline reagents and oxidizing for example: hydrogen peroxide, ozone, per acetic acid, Fenton reaction (Kucharski, 2004; Krzeminska et al., 2013; Kowalczyk et al., 2011; Kim et al., 2009; Dytczak et al., 2007; Saktaywin et al., 2005). During chemical modification of tested sludge the increase or decrease of pH values was observed, which influenced on the changes of physico-chemical properties of sludge. Ions H^+ and OH^- are highly

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toxic to microorganisms living in the excess sludge and observed during the chemical disintegration changes in pH values affect the decline of biological activity of the most microorganisms (Lin et al., 1998; Salyers and Whitt, 2012; Rajan et al., 1989; Penaund et al., 1999).

As a result of chemical pre-hydrolysis followed destruction of cell walls and membranes of microorganisms in the conditioned excess sludge. This causes the release of intracellular material into the liquid sludge. The liquefaction process occurring organic substances contained in sewage sludge has a big influence on the course and efficiency of methane fermentation process, which direct expression is to increase the biogas yield. For the disintegration of the solid fraction the energy is used for organic chemical reactions often associated with the conditions under a reaction, such as temperature or pressure (Zawieja and Wolski, 2013; Zielewicz, 2007; Zawieja and Wolny, 2014).

Hydrogen peroxide used as a reagent of an oxidizing agent has the ability to kill both vegetative and spore forms of microorganisms, it acts strongly against bacteria and viruses. The mechanism of hydrogen peroxide action rely on the active oxygen release, which destroys proteins, lipids and nucleic acids. It has a complete biodegradability in the aqueous medium and high effectiveness in the low temperature. The increase in the dose of hydrogen peroxide increases the efficiency of the oxidation of pollutants should be noted that the H_2O_2 amount is too high in relation to the oxidized substances may act as a scavenger of hydroxyl radicals (Rosinska and Dąbrowska, 2014; Olesiak and Stępniak, 2012; Barbusiński, 2004).

For the oxidation of organic compounds in aqueous solutions are applied methods known as advanced oxidation AOPs (Advanced Oxidation Processes). A characteristic feature of these methods is to generate in the reaction of hydroxyl radicals, included the most powerful oxidants (oxidation potential of 2.7 mV). As indicated by the published literature, the oxidation of organic compounds in the conditions of advanced oxidation is an extremely effective way to remove them from aqueous solutions. Hydrogen peroxide is an ecologically preferred oxidizing agent. The decomposition products of hydrogen peroxide are oxygen and water only (Dabek et al., 2011; Krzemieniewski et al., 2003; Lucas and Peres, 2005).

The aim of this study was to determine the impact of the disintegration process with selected chemical reagents to increase the concentration of organic substances in dissolved form.

2. Material and methods

The tested substrate was excess sludge, which was sampled from the Municipal Wastewater Treatment Plant. Sludge applied for the research was taken immediately before mechanical compaction. The VSS of sludge was 11 g/dm^3, while the COD concentration and VFAs respectively 105 mg O_2/l and 75 mgCH_3COOH/l. The following physico - chemical designations were made: pH by PN-9/C-04540/05, the VSS by PN-EN-12879, volatile fatty acids by steam distillation according to PN-75/C-04616/04 and soluble chemical oxygen demand (SCOD) by dichromate method, using a colorimetric spectrophotometer Hach Dr 400 according to PN-74/C-04578/03. In the tests were used also acidic reagents i.e. HCl (1 M), H_2SO_4 (1 M), alkalies i.e.: $Mg(OH)_2$, $Ca(OH)_2$ (AR) or the oxidative i.e·H_2O_2 (30%). Chemical disintegration time was 2, 6 h and 24 h.

Disintegration of the sludge by thermal method was carried out in a water bath shaker with ELPIN+ type 357. The excess sludge was placed in laboratory flasks with an active volume of 0.5 dm^3, protected against air access by a glass stopper with a manometric tube and heated at a preset temperature for a predetermined preparation time. In the case of chemical disintegration, the mixture of sludge, together with the appropriate reagent dose, was placed in laboratory flasks, the content of which were mixed during the assumed period by placing it in a shaker. Chemical modification was carried out at ambient temperature.

In the case of an oxidizing reagent the COD value was corrected with the value derived from the dose of hydrogen peroxide introduced to tested sludge. It was assumed the complete biodegradability of hydrogen peroxide. The relationship respectively 1 mg H_2O_2 = 0.25 mg O_2 was benefited according to the literature data (Talinli and Anderson, 1992). The disintegration degree was estimated according to the formula 1. The sludge was conditioned by means of 1-mol solution of NaOH for 10 min, at the temperature of 90 °C, with unchanged volumetric proportion of the sludge and the solution (1:1). For sludge pretreatment in accordance with the above methodology the chemical oxygen demand was equal 8875 mg O_2/l.

The degree of disintegration was estimated according the following formula (Zielewicz, 2007):

$$DD_{COD} = (SCOD_1 - SCOD_2)/(SCOD_3 - SCOD_2)\cdot 100 \quad (1)$$

where:

DD_{COD} – disintegration degree,%,
$SCOD_1$ – SCOD level in the pretreatment sludge, mgO_2/l,
$SCOD_2$ – SCOD level in the non pretreatment sludge, mgO_2/l,
$SCOD_3$ – SCOD level in the sludge conditioned chemically 1-mol NaOH with ratio 1:1, temp. 90 °C for 10 min, mgO_2/l.

3. Results and discussion

Subjecting the tested sludge to chemical disintegration using alkalies, acids and oxidizing agent it was observed the increase of organic compounds concentration in dissolved form. Research conducted by Yunqin et al. (2009) and Braguglia et al. (2012) confirmed that a significant impact on the degree of disintegration is the type of chemical reagent, the dose and time of action.

In order to assess the effectiveness of the process using a range of doses of the reactants during the preparation time of 2, 6, 24 h. In the case of modifications carried out using selected reagents received a significant increase in the sludge disintegration. A higher degree of disintegration of the sewage sludge indicates a strong reactivity of selected compounds. It was observed that the extension of the disintegration time does not significantly affect both the efficiency of acidic, alkaline hydrolysis and, when using hydrogen peroxide, oxidation process.

Tables 1–3 show the changes in the content of selected physico-chemical determinations of tested sludge during chemical disintegration with selected acidic reagents i.e. HCl, H_2SO_4 in the time of 2, 6, 24 h.

The highest dose of the used reagent disintegration by hydrochloric acid for 2, 6 and 24 h resulted in growth of supernatant liquid COD value respectively to 3240, 2450, 2718 mg O_2/l. VFAs concentration was 375, 387, 305 mgCH_3COOH/l. In contrast, modification of sulfuric acid for 2, 6 and 24 h resulted the increase of COD in the supernatant liquid of 105 mg O_2/l respectively to 3393, 3338, 3054 mg O_2/l. VFAs concentration was 385, 442, 274 mgCH_3COOH/l. Moreover with the increase of doses of reagent the decrease of pH value was observed.

The value of the disintegration degree of chemically modified sludge by acidic reagents i.e. HCl, H_2SO_4 is shown in Fig. 1.

The highest degree of disintegration of the excess sludge modified by hydrochloric acid and sulfuric acid of about 36% and 37% was obtained respectively with a dose of reagent of 15.0 mg/l and time 2 h. The lowest degree of disintegration for dose of NaOH equal 1.0 mg/l and the pretreatment time 6 h was 10%, while for the dose of KOH equal 1.0 mg/l and the pretreatment time of 2 h it was 13%.

Tables 4–6 show the changes in the content of selected physico-chemical determinations of tested sludge during chemical disintegration with selected alkali reagents i.e. $Ca(OH)_2$, $Mg(OH)_2$ in the time 2, 6, 24 h.

In the case of alkalies with two hydroxyl groups i.e. $Ca(OH)_2$ and $Mg(OH)_2$ for the doses of 10 mg/l and 15 mg/l the similar values of COD and VFAs were obtained. For the $Ca(OH)_2$ and the 2, 6 and 24 h of pretreatment for doses 10 mg/l and 15 mg/l COD value was equal