ISWEE’11

Effects of Heat Treatment and Hydrogen Peroxide (H$_2$O$_2$) on the Physicochemical and Rheological Behavior of an Activated Sludge from a Water Purification Plant

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Abstract

In this work we describe the effects of heat treatment and of the addition of hydrogen peroxide on the physicochemical and rheological behavior of activated sludge produced in a water purification plant. An increase in temperature and dosing with H$_2$O$_2$ both induce a reduction in Chemical Oxygen Demand (COD) of the sludge. At the same time they cause a reduction in the ratio between volatile matter in suspension and total suspended matter (VM/SM). To describe the rheological behavior of the sludge, the Bingham model was used for modeling the viscoelastic behavior of the sludge. The non-Newtonian parameters of the Bingham model decreased with increasing temperature, and at the same time the apparent viscosity of the sludge decreased according to an exponential law.

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Keywords: Activated sludge, temperature, rheological behavior, yield stress, viscosity

Nomenclature

COD    chemical oxygen demand
H$_2$O$_2$ hydrogen peroxide
SM     suspended matter
T      temperature
$V_e$  volume of liquid sample
$VM$   volatile matter in suspension
$\dot{\gamma}$ shear rate

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1. Introduction

The wastewater resulting from various urban activities cannot be directly released back to natural environment because they contain various pollutants, including organics and minerals causing potential various types of diseases. Instead, wastewater must be purified prior to its release, which leads the production of waste sludge. A large quantity is produced from a wastewater treatment plant. An activated treatment of sewage wastewater also results in the generation of a considerable amount of excess sludge. This sludge must be disposed of safely. Commonly used disposal practices comprise of incineration, landfilling and application. The cost for sludge treatment is highly dependent on the volume and water content of the produced waste sludge. Treatment and disposal of an excess sludge in a biological wastewater treatment system requires a very high cost which accounts for approximately 35–60% of the whole operation cost of a wastewater treatment [1].

Various studies have reported the use of different physical, chemical and biological processes to reduce a sewage sludge production. Several disintegration methods have been investigated such as mechanical treatment using ultrasounds [2, 3], chemical treatment using ozone [4, 5], acid or alkali [6], biological hydrolysis with or without enzyme addition. An alkaline hydrolysis was traditionally studied for the sludge reduction and the enhancement of sludge biodegradability. Ozone oxidation is one of powerful sludge destruction process while the cost to disintegrate the sludge through a chemical treatment is typically more expensive than through physical or biological treatment processes. Recently, some researchers reported a process combined with biological process to minimize a sludge production. A combined system of an activated sludge process and an ozone oxidation for excess sludge reduction has been thus successfully developed [7, 8, 9].

The biological hydrogen production from anaerobic fermentation of organic wastes has been proposed as an economical and sustainable technology for both pollution control and clean energy generation [10]. In acid organic hydrogen production process, majority of the removed organic matters is converted to hydrogen, carbon dioxide, and volatile fatty acids. This anaerobic hydrogen-producing process is greatly influenced by many factors, such as substrate composition, substrate concentration.

Concerning the rheological behavior of the sludge several studies have focused on the rheological properties of activated sludge [11, 12, 13, 14] including the effects of suspended matter [15]. It was found [16] that rheological parameters could be used as operating guides for conditioner assessment and control of sludge disposal. [17, 18] have shown that the area of the hysteresis loop on the rheogram could be used as a parameter for indicating overgrowth of filamentous bacteria species in activated sludge. [19] Has extensively studied the effects of surface physicochemical properties of activated sludge on its rheological parameters such as yield stress.

The objective of this study is to investigate the impact of heat and hydrogen peroxide treatments on the physicochemical and rheological behavior of activated sludge produced by an urban wastewater plant.

2. Materials and methods

2.1. Sludge sampling

The sludge sample was collected from the secondary settling tank of a municipal wastewater treatment plant located in Mascara (Algeria) after activated sludge treatment process. The samples were stored at 4°C in a
refrigerator. They were then transported to the laboratory within 24h and they were in the freezer at -20°C in order to avoid changes in the characteristics of the sludge [20, 21].

2.2. Heat treatment effect

The sludge was heat-treated in batches using a water bath containing a borosilicate beaker of one liter capacity with two openings, one for measurements of the temperature of the treated sludge and the other for removal of the treated sludge. The sludge was stirred mechanically at 300 rpm and maintained at the temperature of interest for 1 h.

Heat treatment was carried out with an initial activated sludge concentration of 12.5 g/L. Three temperatures were chosen for the heat treatment: 80°C, 95°C, and 105°C. The duration of heat treatment was 60 minutes. The beaker containing the sludge was introduced in the water bath when the temperature of the water reaches a constant value. A volume of 50 ml of treated sludge was taken every 10 min using a syringe, and was cooled to 20°C during 1 h. The COD, pH, and ratio of volatile matter to matter in suspension (VM/SM) were then measured.

2.3. Treatment by H2O2

The treatment by H2O2 was investigated with a concentrated sludge to obtain a concentration of 16.5 g/L of suspended matter per liter of water. The pH was adjusted to a value of 3 with addition of sulfuric acid 1M. The oxidation of H2O2 was catalyzed with Fe2+ and Fe3+ for treating waste water containing organic matter [22]. This treatment was performed at ambient temperature and pressure with the addition of 0.137 g FeSO4, and a dose H2O2 from 5 to 25 g per kilogram of suspended matter in sludge under a continuous magnetic stirring during 60 min. This treatment method is known as the Fenton process [23].

2.4. Sludge characterization

The matter contained in the various fractions was determined according to standardized method NFT 90.105 [24]. A volume of liquid (Ve) sample was centrifuged for 10 min at 4000 rpm. The pellet was recovered, transferred to a porcelain capsule (W1) and then placed in a drying oven at 105°C for 24 hours in order to obtain the suspended matter. This dried sample was cooled at room temperature, and then placed in desiccators, before being weighed (W2). Subsequently, it was heated in a furnace for 2 hours to burn the volatile matter in suspension. After cooling, the sample was again weighed (W3). The suspended matter (SM) is related to the volatile matter (VM) by:

\[ SM = \frac{W_1 - W_2}{Ve} \]  

2.5. Determination of Chemical Oxygen Demand (COD)

The organic matter in samples of treated and untreated sludge was oxidized in acidic medium (H2SO4) in the presence of a catalyst (Ag2SO4) by potassium dichromate (K2Cr2O7), introduced in excess. After two hours heating at 105°C, the COD was determined by back titration and addition of an ammonium and ferro-iron solution (0.1N Mohr’s salt) at a volumetric dose to the excess potassium dichromate. The COD measurement was used to quantify the pollution.

2.6. Rheological behavior of activated sludge

Stress controlled rheometer RS600 from ThermoFischer equipped with a double coaxial cylinder was used for rheological characterization of the activated sludge. The shear rate was varied linearly form 0.001 s⁻¹ to 200 s⁻¹ during 5 min at different temperatures ranging from 5°C to 50°C.
3. Results and discussion

3.1. Heat treatment effect on the pH of the activated sludge

For these tests, pH was not measured during heat treatment of the sludge but rather before and after treatment at room temperature. Whatever the temperature of heat treatment is, the pH increases with time (Fig. 1). However this increase is much softened for the highest temperature (105°C). [25] Explained this pH increase by protein desorption, which results in the presence of carboxyl groups.

![Fig. 1. Variation of the pH as a function of the thermal processing time at different temperatures of heat treatment](image1)

3.2. Mineral matter solubilization of sludge

To characterize the evolution of the mineral and organic fractions of the sludge, we analyzed the time evolution of the ratio of volatile matter (VM) in suspension by suspended matter (SM) computed from equations (1) and (2) respectively for the different temperatures of heat treatment. The results are shown in Fig. 2.

![Fig. 2. Ratio of volatile matter in suspension (VM) by suspended matter as a function of time at different temperatures of heat treatment](image2)
The ratio VM/SM was approximately 0.94 for the initial sludge, in which the percentage of mineral matter is high. During heat treatment, the ratio VM/SM decreases to 0.28.

A comparison of the obtained ratio VM/SM, in the absence of mineral solubilization, with that observed, allows the degree of solubilization of the mineral matter to be determined. The percentage of VM/SM would thus shift from 94% to 28% if no mineral matter solubilization took place. Heat treatment yielded to a light, clear solubilization of the mineral matter of the floc however the rate of solubilization of organic matter is higher than that of mineral matter. According to [26] there is significant growth of the mineral fraction contained in the floc. This observation is valid regardless of the treatment temperature.

3.3. Heat treatment effect of the solubilization the COD

The chemical oxygen demand of treated sludge $COD_T$ and the chemical oxygen demand of untreated sludge $COD_I$ were determined for each temperature at different times of heat treatment. As seen in Fig.3, $COD_T$ changed depending on the treatment. Thus, for a temperature of 95°C, it remained constant after 40 min of treatment whereas for the other temperatures there was a consistent reduction in $COD_T$. This loss was related to the fact that part of sludge stuck to the walls of the thermal reactor but it was impossible to determine the exact quantity of lost matter. Heat treatment involves a solubilization of the COD.

![Fig.3.Total COD as a function of thermal processing time at different temperatures of heat treatment](image_url)

The results can be analyzed in terms of efficiency defined by:

$$\eta_e = \left(1 - \frac{COD_T}{COD_I}\right) \times 100$$  \hspace{1cm} (3)

It is clear (Fig.4) that the highest efficiency is obtained for 95°C. This temperature is then highly effective at decreasing the COD of activated sludge.
3.5. Effect of the temperature on the rheological behavior of activated sludge

The variation of the shear stress $\tau$ as a function of the shear rate $\dot{\gamma}$ at different temperatures (Fig. 5) clearly shows a Non-Newtonian behavior after a small yield stress. Therefore experimental data were fitted to the classical Bingham model:

$$\tau = \tau_B + \eta_B \dot{\gamma}$$  \hspace{1cm} (4)

where $\tau_B$ and $\eta_B$ are the Bingham shear stress and the Bingham viscosity respectively.

Fig.5. Shear stress as a function of shear rate at different temperatures. The solid lines correspond to the curve fitting to Eq.3.

Fig.6 and 7 shows respectively the evolution of Bingham shear stress and the Bingham viscosity as a function of temperature.
A decrease exponential law can describe the variation of shear stress ($\tau_B$) and Bingham viscosity ($\eta_B$) as a function of temperature. This behavior sludge can be explained by the solubilization of the exopolymer. [27] Studied the effect of temperature on liquid waste sludge. The samples tested were maintained at 10, 15, 20 and 25°C At these temperatures, the authors observed that the apparent viscosity of the sludge varied in proportion similar to that of a Newtonian fluid. Indeed, high temperature modified the structure of sludge by solubilizing the matter. Thus, an increase in temperature facilitates transport of the sludge through the conduits of the pumping stations.

3.6. Effect of treatment by $H_2O_2$ on the chemical oxygen demand (COD)
It is clearly seen that the chemical oxygen demand of treated sludge $COD_T$ decreases with an increase of hydrogen peroxide dose (Fig. 8). A possible explanation is the increase in the solubilization of the particulate matter. The addition of $H_2O_2$ will oxidize the organic matter in the form of $CO_2$ and $H_2O$, therefore the quantity of the reduced organic matter at summer.

![Figure 8](image1)

**Fig. 8.** Effect of treatment by $H_2O_2$ on the COD of sludge

The decrease of $COD_T$ with the addition of $H_2O_2$ can be expressed as for heat treatment in terms of COD effectiveness which increases from 12% to 45%. (Fig. 9).

![Figure 9](image2)

**Fig. 9.** Effect of the treatment by $H_2O_2$ on the effectiveness of the COD

3.7. Solubilization of the mineral matter of sludge by $H_2O_2$

The VM/SM ratio decreases linearly with an increase of the dose of $H_2O_2$ (Fig. 10) from 55 for untreated sludge to 16% for the treated sludge. This reduction in VM/SM ratio involves a modification of the final composition of sludge which must be taken into account for their incineration or their spreading. Indeed, a reduction in the content
of organic matter of final sludge induces a reduction of their calorific power and an increase in the salt concentration.

Fig.10. Ratio VM/SM as a function of the dose in H$_2$O$_2$

4. Conclusion

We evaluated the impact of heat and hydrogen peroxide (H$_2$O$_2$) treatments on chemical oxygen demand, pH, mineral matter solubilization and shear rheological properties of activated sludge collected from urban wastewater plant.

In the studied temperature range, the 95°C heat treatment led to the highest efficiency of chemical oxygen demand of the activated sludge.

The addition of H$_2$O$_2$ led to a linear decrease of the ratio of volatile matter by the suspended matter and to a linear increase of the efficiency of chemical oxygen demand from 12% to 45%. These behaviors could be associated to the degradation of organic matter.

A good fitting of shear thinning behavior of activated sludge was achieved with Bingham model. An exponential relationship was found between temperature and the Bingham’s rheological parameters (yield stress and Bingham viscosity). The decrease of these two parameters with temperature is a key factor for facilitated transport of the sludge into the conduits of the pumping stations, providing further evidence of the advantage of heat treatment.

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