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Studies on treatment of bitumen effluents by means of Advanced Oxidation Processes (AOPs) in basic pH conditions

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Summary
The paper presents the results of studies on chemical treatment of effluents from production of bitumen of petroleum origin. Due to the presence of sulfide ions, the pH of these effluents is strongly alkaline. Several Advanced Oxidation Processes (AOPs) were studied, including the use of hydroxyl and sulfate radicals oxidants, the hydrodynamic cavitation as well as sonocavitation. The best processes allow to obtain 45% reduction of chemical oxygen demand value (COD) along with effective degradation of the majority of the volatile organic compounds present in the effluents. Some of the studied processes, especially the one using sonocavitation revealed to produce high amounts of VOCs by-products.

Wastewater treatment; AOP; Cavitation; VOC; Bitumen

1. Introduction

Petroleum or refinery effluents are well known to be highly polluted and to contain several groups of organic compounds, including a significant amount of volatile organic compounds (VOCs) [1,2]. A particularly important group of refinery effluents are produced in an alkaline medium, like spent caustic [3] and post oxidative effluents [4]. This strong alkaline pH results from the need of quantitative absorption of hydrogen sulfide, present in the form of S^{2-}. The pH correction to neutral or acidic values is not preferred due to the production of hydrogen sulfide which can be emitted to the atmosphere. Such effluents have also a high total load of organic pollutants and can't be purified directly by biological wastewater treatment processes. Therefore effective, alternative, easy and cheap technologies are needed to treat these sewages at their natural pH in order to reduce their toxicity and even to increase the range of pH where such effluents can be treated.

This paper is focused on the comparison of a few alternative Advanced Oxidation Processes (AOPs) effectiveness in the treatment of effluents from production of bitumen (a post-oxidative effluents). The production of bitumens involves oxidation of residue from vacuum distillation of crude oil to obtain products with desired properties. During operations yielding the raw material for bitumen production (vacuum distillation) as well as the process of oxidation with hot air, the bitumen mass deposited on heating elements undergoes partial thermal cracking, which results in the formation of unsaturated and aromatic compounds as well as hydrogen sulfide, water vapor, carbonyl sulfide, carbon disulfide and others. These compounds undergo further transformations yielding a variety of volatile compounds: ketones, aldehydes, organic acids, phenols and their derivatives, as well as organosulfur and organonitrogen compounds. A fraction of the resulting volatile compounds is removed from the reactor with hot air, yielding so-called exhaust gases, which undergo scrubbing in a basic aqueous solution or absorption in wash oil [4]. If the scrubbing of waste-gases is made using the aqueous solution (mainly of sodium hydroxide), a specific effluents from bitumen production are formed (a so-called post-oxidative effluents). Such effluents contain a condensed oil phase (removed by plate-separator), sulfide ions and organic compounds dissolved in the water phase. Such stream are an interesting subject of the research in the field of WWT but also on the chemical composition of the effluents as well as the pathways of oxidation of selected groups of compounds during chemical treatment.

The studied AOPs include non-catalytic and catalytic oxidation using hydrogen peroxide, ozone and sulfate based oxidants with connection of photooxidation processes as well as cavitation phenomena. The use of cavitation phenomena for wastewater treatment (WWT) is a promising approach and in this studies a two groups of such processes – hydrodynamic cavitation and sonocavitation were studied. A recent study revealed that classic AOPs using ozone were more effective than other processes in the treatment of model and real WW at basic conditions. In addition the sulfate radical based AOPs can include a wider pH range of treatment and further studies on real WW is suggested [3]. We are a first research team, that studies this type of industrial effluents. Surprisingly, such interesting industrial and environmental issue never earlier has been discussed in the scientific literature.

2. Materials and methods

2.1 Materials

In this studies a real post oxidative sewages from bitumen production plant from Lotos Asfalt (Grupa Lotos, Poland) were used (COD - within the range of 18.000-22.000mg/L; BOD within the range of 5000-6000mg/L, pH 10.5.). Hydrogen Peroxide 30%, Sodium Sulfite nonahydrated ($Na_2S.9H_2O$), Sodium Persulfate ($Na_2S_2O_8$) and Potassium Peroxymonosulfate ($KHSO_5$) were purchased from POCH Poland.

2.1.2 AOP apparatus

The studies were performed using a three large-laboratory scale installations, 1 a one using a tank reactor for classic AOPs (fig. 1)

Fig. 1 A batch reactor for classic AOPs. 1- reactor, 2 – control panel (mixing and temperature), 3 – pump for oxidant, 4 – ozonator, 5 – pump for effluents

(2) a second one for hydrodynamic based AOPs (fig. 2)

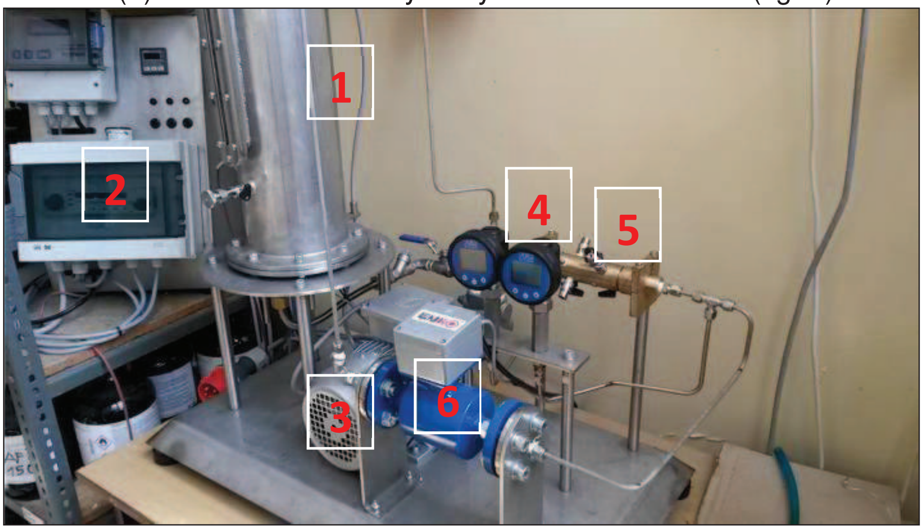

Fig. 2 A hydrodynamic cavitation reactor. 1- effluent tank, 2 – control panel (mixing, temperature, volumetric flow), 3 – pump for effluents, 4 – pressure control, 5 – Venturi tube, 6 – flow control.

(3) a third one for sonocavitation based processes (kindly provided for this research by Bandelin company). (Fig. 3)

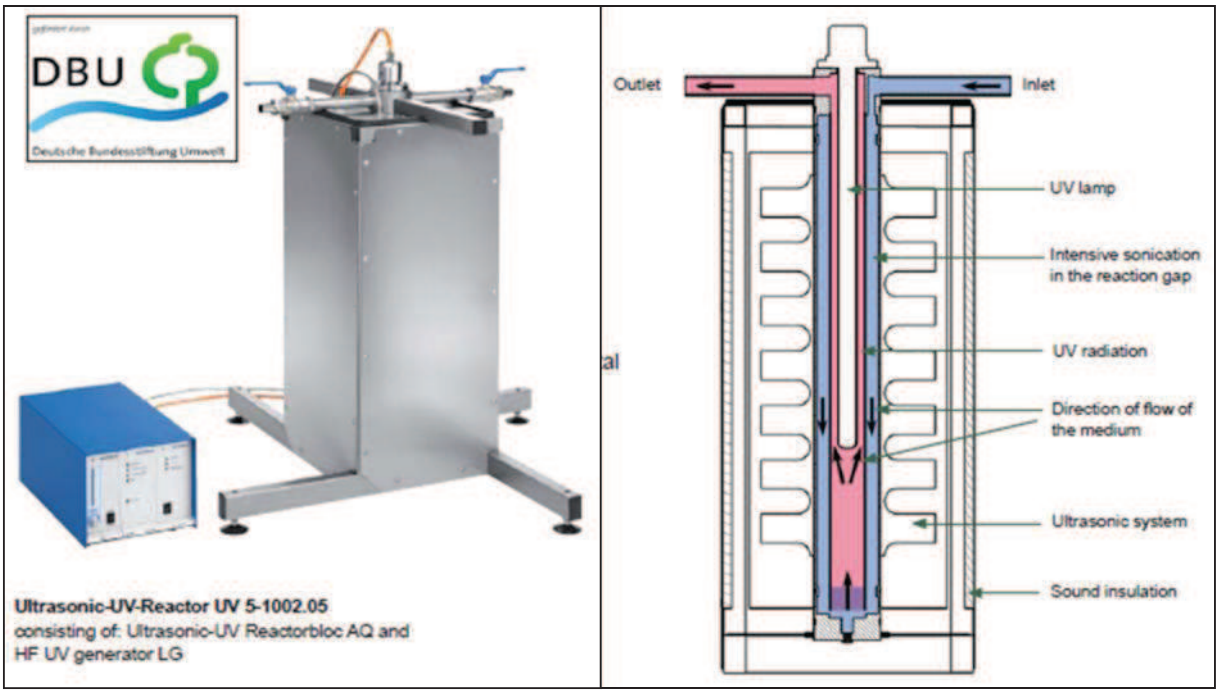

Fig. 3 A Sonocavitation reactor.

The equipment used for the process analytics is fully described in our previous papers [4-8].

2.2 Methods

2.2.1 Sewage treatment

In every procedure, a volume of 5 dm^3 was used. For reactor (1) the sewages were pumped to the reactor, working in a batch mode. The installations (2) and (3) were operated in batch mode with recirculation of the effluents through a sonocavitation or hydrodynamic cavitation chamber.

All procedures were done at an initial pH of 10.5. Regarding the oxidant dose, the flowrate was established depending on the ratio between the oxygen (O_2) added from the oxidant source and the COD in the sewages (r_{ox}). Samples with a total volume of 0.022 dm^3 were taken before the beginning of treatment, 15 minutes in the first hour of treatment, at 90 minutes,120 min, and every hour after 120min and at the end of the treatment. The treatment time depended on the r_{ox}. The pH was measured by pH strips in every sample taken.

2.2.2 Process analytics

All analytical methods used in these studies are described in details in our previous papers [4-8]. Generally, the COD, BOD and Sulfides were controlled by standard test methods. VOCs were analysed by means of gas chromatography (GC) with selective detectors as well as mass spectrometry (MS)

3. Results and Discussions

The effluents from a bitumen production were submitted to treatment by various types of AOPs . The parameters under study were the influence of the oxidant to COD ratio (r_{ox}), the type of oxidant and the temperature of the process on the degradation effectiveness (for batch mode reactor). For hydrodynamic cavitation processes the results of treamtnet were also compared with cavitation number. The parameters used for determining the efficiency of the treatments were COD, BOD, [S^{2-}] and selected groups of VOCs such as oxygen containing (O-VOCs), sulfur (VSCs) and nitrogen (VNCs) controlled by GC technique.

The studies revealed that in the case of "classic" AOP (non-cavitation assisted) peroxone (a H_2O_2 and O_3 introduced in the same time) at 40 ºC achieved 43% and 36% of COD and BOD removal resulting to be the most effective studied AOP from this group. The used r_{ox} was 1.02. In all studied processes the sulfide ions were quantitatively oxidized in the first 15min of treatment. Regarding the volatile sulfur compounds (VSCs), they achieved high degradation removals, with values after treatment bellow the limit of detection values of used analytical methods. In the case of O-VOCs and VNCs some compounds were identified as a secondary pollutants, which concentration was inreasing during the treatment.

In the case of sulfate radicals AOPs (S-AOPs), peroxymonosulfate with a r_{ox} of 1.43 at 60 ºC achieved 43% COD and BOD removal resulting to be the most effective AOP studied. These type of oxidants can be activated by the temperature of the medium, thus the amount of sulfate radicals available for reaction with pollutants is increased at elevated temperatures. Persulfate is more effective for studied purpose than peroxymonosulfate in terms of r_{ox} and temperature. This results mainly from higher Eº value of persulfate. In comparison with classic AOPs persulfate and peroxymonsulfate achieved higher degradation but needed higher r_{ox}.

The sole use of cavitation phenomena (induced by flow or ultrasounds) for degradation of chemical compounds present in the effluents from bitumen production allows to lower the COD by 13%. The hydrodynamic cavitation allows to degrade more efectively VOCs, but what is more important – without production of new volatiles as by-products. Coupling cavitation with oxidation by external oxidants allows to lower the COD by approx. 44%.

In overall, in most of the studied processes a high degradation of VOCs was achieved. The studied AOPs effectively reduce the total load of pollutants but also allow to decrease the total content of volatile organic compounds. This is particularly important and have a practical value – it lowers the malodorness of the sewages. It is important in the case of next stages of treatment which are mainly the biological processes. The biological stage is often performed at open-air reservoirs, which causes emission of VOCs to the atmosphere. The decrease of content of VOCs as well as the decrease of total load of pollutants makes the studied processes have applicational value for real wastewater treatment plants.

4. Conclusions

Effluents from bitumen production are an interesting type of wastewater. They contain a wide variety of organic compounds as well as sufide ions, and from that reason the chemical treatment must be performed in strongly basic pH. The studies revealed, that it is possible to pre-treat this effluent with effectiveness up to 45% in respect to COD. Further increase of degradation is hard to obtain due to the presence of hydrocarbon type compounds which a persistent to degradation in the studied conditions. A comparison of processes revealed significant changes in respect to degradation of selected VOCs as well as possibility of by-products formation.

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