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BASIC STUDY OF ADVANCED PHOTOOXIDATION OF SURFACTANT IN WASTEWATER

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Abstract

There are several conventional methods used for the removal of surfactants from wastewater, but they are not satisfactory enough for the hardly biodegradable pollutants. It has also been observed that the treatment of surfactants usually requires periods of long acclimation and it typically results in a quite incomplete degradation. Advanced Oxidation Processes (AOP), promising techniques because of their capability to mineralize completely recalcitrant water, air or soil contaminants into CO₂, H₂O and small amount of simple inorganic compounds, have received much attention recently. Heterogeneous photocatalysis, being one of AOP, is an efficient and economic method that can be used in the decomposition of hazardous pollutants, because it is able to mineralize almost all organic compounds only by means of atmospheric oxygen at the ambient conditions of temperature and pressure. It was observed that the heterogeneous photocatalysis can be applied for the surfactants removal from the wastewater successfully.

Index Terms: acclimation, recalcitrant etc.

1. INTRODUCTION

There are several conventional methods used for the removal of surfactants from wastewater, but they are not satisfactory enough for the hardly biodegradable pollutants. It has also been observed that the treatment of surfactants usually requires periods of long acclimation and it typically results in a quite incomplete Degradation.

1.1 General Introduction to Surfactant

Surfactants are commonly used in the households as detergents, or care products; their specific features make them become useful Also in various industries: in pesticides, pharmaceuticals, textile and others. All of these have resulted in their common presence in the Wastewater. According to various studies and different tests, it has been confirmed that non-ionic surfactants (at lethal concentrations: 0.0025 to 300 mg/dm³) are more toxic than others (anionic: 0.3 to 200 mg/dm³). Some of surfactants, however, can be successfully used for soil-washing or soil-flushing pump-and-treat Technologies in the surfactant-enhanced remediation, where TX enhances the solubilization of hydrophobic contaminants through Micellar solubilization in soil. For the studies Triton X-100 (TX) as one of the representatives of widely industrial scale used non-ionic Surfactants of alkylphenylpolyoxytype was chosen. Alkylphenyl Compounds are suspected to be the endocrine disrupters in aquatic Organisms.

1.2 General Introduction to Advanced Oxidation

Advanced Oxidation Processes (AOP), Promising techniques because of their capability to mineralize completely recalcitrant water, air or soil contaminants into CO₂, H₂O and small amount of simple inorganic compounds, have received much attention recently.

Heterogeneous photocatalysis, One of AOP, is an efficient and economic method that can Be used in the decomposition of hazardous pollutants, because it Is able to mineralize almost all organic compounds only by means Of atmospheric oxygen at the ambient conditions of temperature And pressure.

It was observed that the heterogeneous Photocatalysis can be applied for the surfactants removal from the wastewater successfully.

TiO₂, among other widely tested semiconductors, seems to be the most suitable for both fundamental research and practical applications, as it is chemically and biologically inert, photo stable, non-toxic, Affordable, cheap and has high oxidative power.

The detailed Mechanism of photocatalysis over TiO₂ surface is well known and Involves the generation of high energy electron-hole pairs and their Reactions with organic molecules adsorbed on the surface or oxygen yielding the formation of OH radicals.

The radicals react non-selectively and quickly with the organic molecules leading to their mineralization.

2. EXPERIMENTAL STUDY

2.1 Preparation of The Photocatalysts

All the chemicals were analytical grade and used without further purification. The modified TiO_2 catalysts supported by $\gamma\text{-Al}_2\text{O}_3$ were chosen for the studies. The support, being in a form of beads with the diameter ca. 3 mm and BET surface area of $150 \text{ m}^2/\text{g}$, was treated in the proper solution of TiCl_4 (Sigma-Aldrich) dissolved in the aqueous solution of concentrated hydrochloric acid for 10 minutes at the room temperature. After the impregnation of the support, the sample was dried at 388K for 2 hours and calcinated at 873K for 3 hours.

The application of TiCl_4 is connected with the presence of the Cl^- on the surface of the catalysts, though the catalysts were washed with the water until the reaction of Cl^- with AgNO_3 was not observed.

CIM was carried out as follows: the obtained $\text{TiO}_2/\text{Al}_2\text{O}_3$ support was impregnated with 5 wt. % aqueous solution of nitrates: $\text{Zn}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ (poch, Gliwice, Poland) (samples CIM-Zn and CIM-Cu respectively). On the basis of the pure metal the amount of salt was calculated. The process of impregnation lasted 9 minutes.

For DIM, the titanium-alumina support was initially impregnated with 0.1M aqueous solution of EDTA at 343K for 0.5 h. In the second step, the support with the adsorbed EDTA was impregnated with 5 wt. % solution of Cu or Zn for 9 minutes (samples DIM-Cu and DIM-Zn respectively). After they were dry, all the precursors under study were calcinated at 873K for 3 hours.

2.2 Photoreactor and Photocatalytic Studies

The experiments regarding the photocatalytic degradation of organics in the wastewater were conducted in a band reactor of our own construction.

The reactor (Figure 1.) Has a form of two tubes placed above the UV lamp (254 nm, 50 Hz) with the light intensity of $1.56\text{--}2.09 \text{ mw}/\text{cm}^2$, equipped with the Radiometer that was used to measure the emitted light of the applied lamp UV. The employed light source emitted light of more than 95% within the UV light wavelength. The bands, being the main mixing agents, ensure the counter-current contact of the reagents. A mixture of oxygen ($3 \text{ dm}^3/\text{h}$) and nitrogen ($37 \text{ dm}^3/\text{h}$) was introduced into the reactor. Oxygen plays a key role in the TiO_2 photocatalysis, as it is found to be the rate-limiting step.

Triton X-100 (POCH Gliwice, Poland) and a commercially available wash-up liquid were chosen to be the model

2.3 Catalysts Examination

The activity of the photocatalysts has been tested in the removal of TX and wash-up liquid from water. C_0 has been used to calculate the conversion, where C_0 was the initial COD of the surfactant, and c was COD of the compounds under study that did not react at a steady state.

This is studied that the photo removal of TX proceeds mainly over TiO_2 . $\text{Cu-TiO}_2/\text{Al}_2\text{O}_3$ showed the same activity independently from its preparation method. Its

contaminants. The solutions were prepared so as to have the COD value of ca. $3000 \text{ mg O}_2/\text{dm}^3$, which is the concentration of $22.6 \cdot 10^{-4} \text{ mol}/\text{dm}^3$ for TX. The wash-up liquid contained: 5-15% anionic, <5% non-ionic and <5% amphoteric surfactants and many others.

A sample of wastewater was pumped in the reactor with the volumetric flow of $1.3 \text{ dm}^3/\text{h}$ and 20g of the catalyst (e.g. Ca. $8 \text{ g}/\text{dm}^3$) were placed inside. Moreover, H_2O_2 (0.01 vol.%) was used as an additional oxidizing agent.

After 115 minutes, e.g. One complete run through the reactor, the sample was taken out and analysed for COD (Chemical Oxygen Demand) by means of a bichromate method.

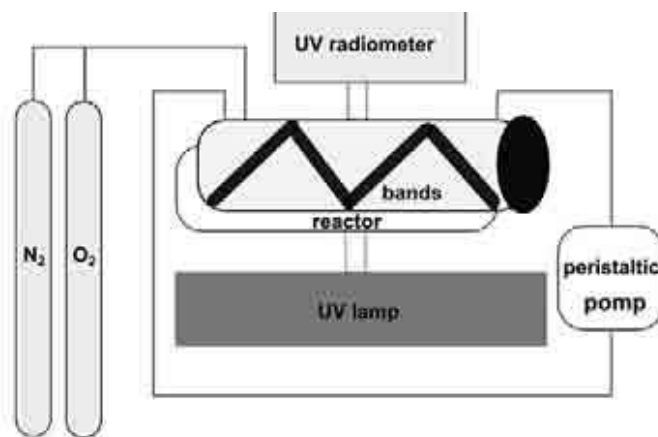


Fig-1: Band Reactor

2.3 Catalysts Examination

The total surface areas of the catalysts were resolved on the basis of nitrogen adsorption at liquid nitrogen temperature using the BET method in a volumetric apparatus ensuring a void of at least $2 \cdot 10^{-6} \text{ kPa}$, the phase composition diagram of the catalysts was resolved. While Raman spectroscopy allowed to show the crystallographic orientation of a sample, the UV-Vis spectroscopy was applied to characterize the absorbance spectra of the photocatalysts. The sample morphology was observed in the scanning electron microscope equipped with an energy dispersive X-ray detector, which was used for the determination of the surface elemental composition. The physicochemical belongings of the studied catalysts are existing in. The photocatalytic activity of the catalysts was estimated for TX and the commercially available wash-up liquid during the photooxidation in the band reactor.

activity, however, is strongly connected with the amount of a dopant by which Cu effectively inhibits the recombination of photoinduced charge carriers. The observed decrease in the removal of TX can be attributed to the excess of Cu when compared with TiO_2 . It has been stated that too high Cu values in the photocatalysts result in the more excessive oxygen vacancies, and thus Cu species become the recombination centers of photoinduced e^-/h^+ . Cu covering the TiO_2 surface can be also noticed.

The synergistic effect of ZnO and TiO₂ semiconductors has not been observed during the removal of COD of waste water containing TX. It can be, however, noticed during the removal of more complicated compositions and compounds e.g. Wash-up liquid. CIM-Zn caused better removal of wash-up liquid than the same photocatalyst prepared by DIM what may suggest that different sites participate in the process or may indicate that TiO₂ has oxidized the non-ionic surfactants and the dopants have facilitated photooxidation of the other wash-up liquid components, even inorganic. That may be in agreement with the literature Data. It was observed only a slightly enhanced photoremoval of methyl orange

over ZnO-TiO₂. However, about 5–8% of the deepened photooxidation using modified photocatalysts has not been economically justified.

3. CONCLUSION

Rendering to the achieved results it may be concluded that:

The addition of H₂O₂ does not cause any significant changes in COD of wastewater during treatment using studied TiO₂ catalysts. It is economically unjustified to conduct the treatment for more than 2 hours. 100% colour and chemical oxygen demand removal. 90% COD reduction is obtained. This method is practically cannot be implemented for large scale water treatment plant.

4. REFERENCES

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