



# The novel method of water purification proces in the fluidized bed reactor with periodic and self regenerating film of $\text{TiO}_2/\text{FAC}$

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## Introduction

The results of the photocatalytic process carried out in the new type of inclined, three-phase fluidized bed reactor with periodic film of photocatalyst are presented. These phases were fly ash cenospheres coated with  $\text{TiO}_2$ , an aqueous solution of methylene blue and an air stream passing from the bottom of the photoreactor, respectively. The cenospheres have a density lower than water, thus it could form catalytic film on top irradiated window. The formed surface film is stable, but easy to break and to reproduce in a cyclic air sparged process. The mixing was provided in the cyclically or continuously manner. From the operational point of view the best variant of mixing was 10 s air sparge/10 s break with 50% duty cycle, because it provided the same discoloration efficiency and reduced to a half energy demand with reference to continuous mixing. The proposed photocatalytic reactor due to film formation allows to substantially reduce the energy demand for the mixing with maintaining the desired degree of discoloration.

## Photocatalytic experiments

The FB-MOCVD (fluidized bed metal-organic chemical vapour deposition) method was used for deposition of active phase onto cenosphere support. The photocatalytic experiments were conducted in the photoreactor (Figure 1(1)), in which side walls were made of the window glass and the front wall was made of quartz glass type JGS2. The volume of the reaction zone (irradiated volume) was about  $160 \text{ cm}^3$ , whereas the total volume of the MB in circuit was  $750 \text{ cm}^3$ . The irradiated area (front wall surface) was about  $133 \text{ cm}^2$ . Cenosphere catalyst was introduced into the reactor in the amount of 0.5, 1 or 2 g, depending on the experiment. Moreover photolysis process without catalyst addition was examined. The MB solution was introduced to the reactor using a peristaltic pump with volumetric rate of  $30 \text{ cm}^3/\text{min}$  via an inlet tube located above the reaction zone (10) and it was drained through an outlet tube (8) terminated with a separator ( $60 \mu\text{m}$  sieve, that separated cenospheres from the solution). The average residence time of the solution in the reactor was about 5 min. Depending on the experiment, the reactor was mixed cyclically or continuously with an air flow of about  $100 \text{ cm}^3/\text{s}$ . Three mixing modes were used: continuous mixing (100% duty cycle – labelled 10/0), 10 s air sparge/10 s break (50% – labelled 10/10), and 10 s air sparge/20 s break (33% – labelled 10/20). Before starting the UV lamp, the system was mixed (in 10 s air sparge /20 s break mode) for about 90 min to establish the sorption equilibrium. Afterwards, the 18W UV-C lamp was turned on (located approx. 5 cm above the reactor) and the proper mixing mode was set. Discoloration of the model sewage during the experiment (every 40 min  $2 \text{ cm}^3$  MB solution was withdrawn from the reactor) was determined by the spectrophotometric method at the wavelength of 665 nm.

## Catalyst's film formation

Figure 2 shows the process of mixing the MB solution with the cenosphere forced by cyclic aeration, as well as the processes of formation and breaking of the catalytic film. The film formation was possible due to the inclination of the reactor (at the angle of  $28^\circ$ ). As a result, the cenospheres initially dispersed in the reaction zone, after the air sparge stopping, had lifted upwards, and had stayed near the inclined wall made of the quartz.

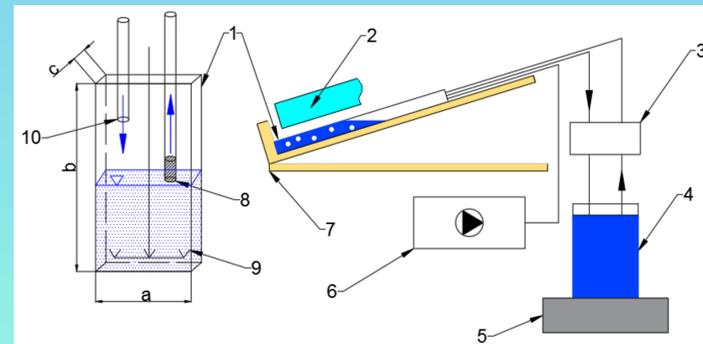


Figure 1. Laboratory system scheme, 1 - air sparged reactor, 2 - UV lamp, 3 - peristaltic pump, 4 - beaker with methylene blue (MB) solution, 5 - magnetic stirrer, 6 - air pump, 7 - frame mounting the reactor, 8 - MB solution outlet, 9 - air sparger, 10 - MB solution inlet, a=63 mm, b=300 mm, c=25 mm.

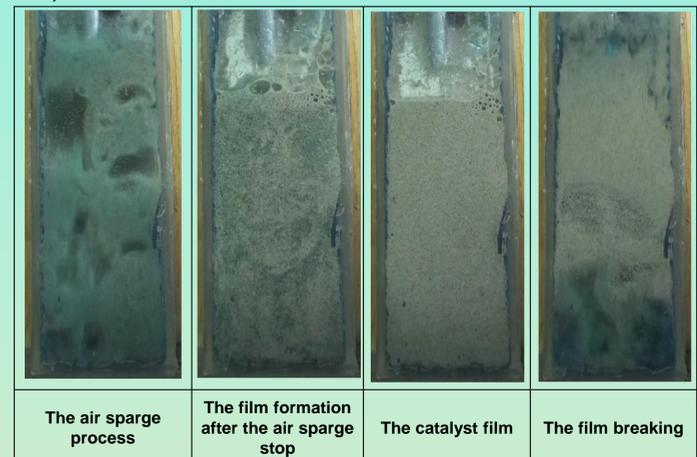


Figure 2. The cyclic process of the catalytic film formation and breaking

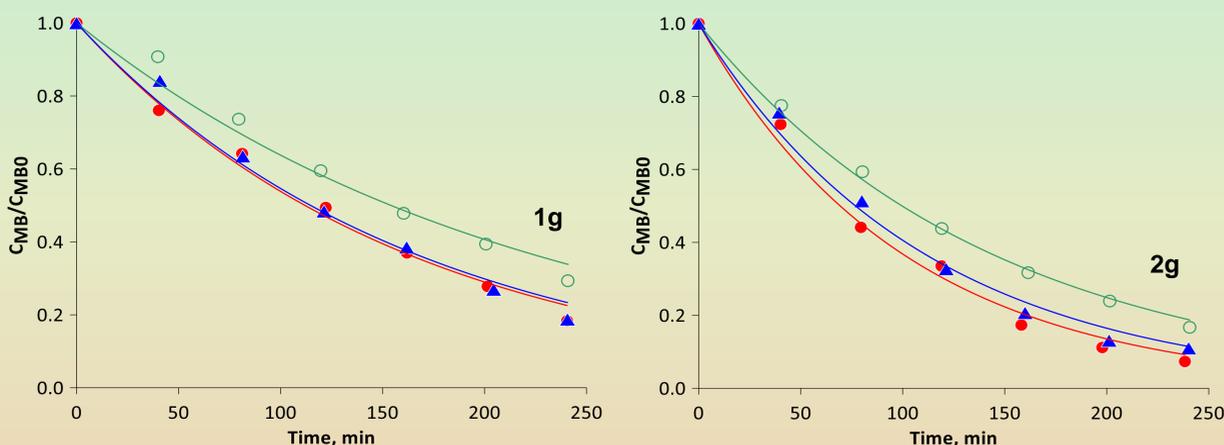


Figure 3. MB Concentration as experimnet's time function,  $\blacktriangle\blacktriangle\blacktriangle$  full time stirred,  $\bullet\bullet\bullet$  10s air sparged/10s break,  $\circ\circ\circ$  10s air sparged/20s break

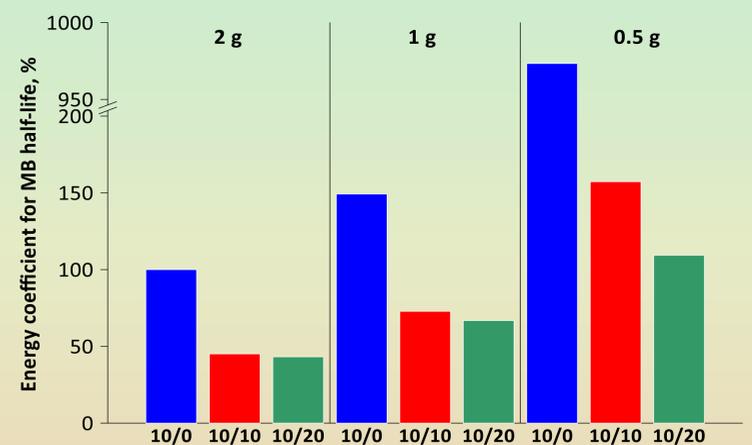


Figure 4. Relative energy demand of mixing process to achieve a 50% dye reduction, depending on the mixing mode (Note: OY axis was broken at 200%).

## Results

Figure 3 presents MB concentration as experimnet's time function (for 1 and 2g of cenospheres catalysts), whereas the relative energy demand of mixing process to achieve a 50% dye reduction, depending on the mixing mode is depicted in the Figure 4. The use of an inclined three-phase fluidized photocatalytic reactor with a periodic mixing of the cenospheric bed allows to reduce the energy cost of the mixing process while maintaining the desired degree of discoloration. Through the cyclical film breaking and formation, the reactor combines the features of a reactor with suspended and immobilized photocatalyst. The catalyst film formation period is characterized by a significant reduction of the solution layer, located between the source of light irradiation and the catalytic surface. As a result, this leads to an improvement in the photocatalyst exposure. Simultaneously, interruption of mixing, leads to a decrease in the rate of mass transfer between the solution and the catalyst surface, thus slowing the purification process. Obtained results proved that the generation of a catalytic film was beneficial, and from the operational point of view the best variant of mixing was 10 s air sparge/10 s break (10/10) with 50% duty cycle. This variant provided the same discoloration efficiency and reduced to a half energy demand with reference to the continuous mixing. The best amount of catalyst was 2 g, because it required about 60% less time or energy to purify the MB solution in comparison to 1 g in the 10/10 mixing mode. However this value is not optimal, because of incomplete (80%) catalyst utilization. On the other hand, utilization of not expensive catalyst, based on waste material as a support enable to usage of higher catalyst amounts with reasonable economical balance.