PHOTOCATALYSIS OF BISPHENOL A IN AQUEOUS SOLUTION BY ZEOLITE/TITANIA COMPOSITES

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ABSTRACT

The composites based on TiO_2 nanoparticles, supported on natural zeolite clinoptilolite (Cli) and synthetic beta (β) zeolite were prepared using simple ultrasound assisted solid state dispersion method and tested for photodegradation of bisphenol A (BPA) in aqueous solution. X-ray powder diffraction (XRPD), UV-Vis diffuse reflectance (DR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy were used for characterisation of the obtained composites. The composite based on β zeolite (Si/Al=19) showed photocatalytic efficiency for removal of BPA comparable to efficiency of TiO_2. Furthermore, composite based on low cost natural zeolite clinoptilolite with addition of H_2O_2 also proved to be effective for photodegradation of BPA.

Key words: photocatalysis, TiO_2, zeolite, bisphenol A, emerging contaminant.

INTRODUCTION

Nowadays, various emerging contaminants are being detected in the aquatic environments because application of conventional wastewater treatments is inefficient for their complete removal. The mass production of bisphenol A (BPA), about three million tons annually, and wide spread use, e.g. as a plasticizer in different man-made products, led to its presence in the surface waters, groundwater and wastewater [1]. Numerous harmful effects of BPA to human body have been proven: endocrine disrupting property, carcinogenesis and epigenetic modifications [1]. Regardless of these facts, BPA is still widely used. Canadian government, European Commission and Food and Drug Administration have forbidden the usage of BPA in the production of certain infant products, yet the presence of BPA in the environment raises serious concerns and requires application of different technologies for its efficient elimination [2].

Advanced oxidation process is a very promising technique that relies on the production of highly reactive species such are hydroxyl radicals, which are able to degrade different organic compounds. TiO_2 based photocatalysis gained a significant attention as an effective and environmentally friendly method for pollutants elimination because TiO_2 nanoparticles have high activity, chemical stability, no toxicity and low price. However, their agglomeration and costly filtration process in wastewater systems represent a drawback in the process. The deposition of TiO_2 on high surface area supports such as zeolites could resolve this issue and also prevent leaching of nanoparticles as there are concerns about toxicity of TiO_2 nanoparticles [3]. Zeolites are compatible materials for photocatalysis which possess photochemical stability, high adsorption capacity and transparency to ultraviolet/visible irradiation [4]. Thus, composites where TiO_2 is immobilised on zeolitic support offer a promising solution as the leaching of nanoparticles is prevented, agglomeration reduced and reusability preserved. Moreover, the removal of pollutants can be obtained through synergistic effect of zeolites' adsorption and TiO_2 photocatalysis [5].

In this study, clinoptilolite was used as a support for TiO_2 nanoparticles because it is affordable and abundant natural zeolite with the purpose of developing economical photocatalyst. For comparison, synthetic β zeolite was also used as a support. In order to

investigate the influence of Si/Al ratio, β zeolite with Si/Al=19 and Si/Al=180 were used. The aim of this study was to test and compare photocatalytic degradation of BPA using composites based on TiO_2 nanoparticles and different zeolites (Cli, β(19) and β(180)).

EXPERIMENTAL

Natural zeolite clinoptilolite (Cli) (Si/Al = 5, Zlatokop mine, Serbia) and β zeolite (Si/Al = 19 and Si/Al = 180, Alfa Aesar) were used as a supports for Aeroxide® (formerly Degussa) P25 TiO_2 nanoparticles from Evonik (denoted as P25). P25 in amounts of 20 wt% were thoroughly mixed with starting zeolites using ethanol in a 10:1 ratio (ethanol ml/solid powder g) and sonicated for 4 h at 80 °C. Afterwards the composites were dried at 80 °C and calcinated in air at 500 °C for 5 h. The materials were labelled as TCli-20, Tβ(19)-20 and Tβ(180)-20 where T stands for TiO_2, Cli and β indicate the type of used zeolite, number in parentheses labels Si/Al ratio and the other number represent wt% of used TiO_2.

XRPD patterns of composite materials were obtained using Rigaku Ultima IV diffractometer (Cu Kα radiation λ=1.54178 Å) with 4° - 50° 2θ range, 0.020° step and 1°/min acquisition rate. UV–Vis diffuse reflectance (DR) spectra of composite materials were recorded on Agilent Cary UV-Vis-NIR 5000 spectrophotometer equipped with an integration sphere (range: 200 - 800 nm, data interval: 1 nm and scan rate: 600 nm min^{-1}). FTIR spectra of composite materials were acquired on Nicolet 6700 FTIR spectrometer (range: 4000 - 400 cm^{-1}, resolution: 2 cm^{-1} and acquisitions: 32).

Bisphenol A (BPA) (2,2-Bis(4-hydroxyphenyl)propane) was purchased from Sigma Aldrich (≥ 99%). The photocatalytic tests were performed with 40 ml of aqueous solutions of BPA containing 1 gL^{-1} of catalyst at room temperature under constant stirring and illumination. In order to reach adsorption-desorption equilibrium, suspensions were stirred for 30 minutes in the dark. The used initial concentrations of BPA were different: 10, 20 and 50 mgL^{-1}. The lamp (Osram Vitalux 300 W) that simulates sun irradiation was used as a light source. The BPA (λ_{max} = 225 nm) concentration was measured using UV-Vis spectrophotometer (Thermo scientific evolution 220) ranging from 200 to 400 nm.

RESULTS AND DISCUSSION

XRPD patterns of P25, starting zeolites and investigated composite material are shown in Fig. 1. Peaks in diffractogram of natural zeolite Cli correspond to characteristic reflections of clinoptilolite mineral and to photocatalytically inert impurities of quartz (2θ = 20.8°, 26.7°) and feldspar [6].

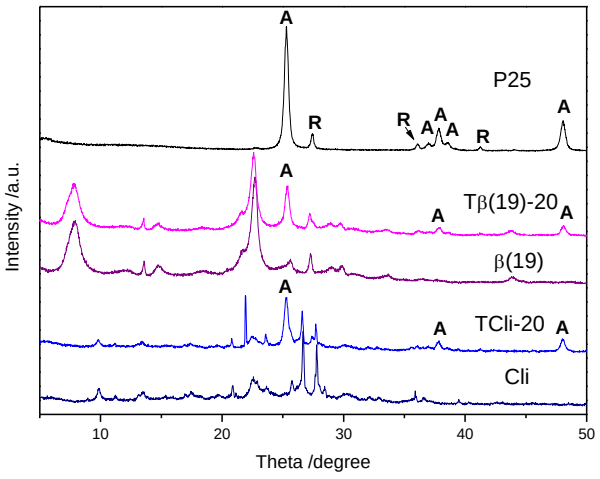

Figure 1. XRPD patterns of P25, starting zeolites (Cli and β(19)) and composite materials (TCli-20 and Tβ(19)-20). Abbreviations: A-anatase and R-rutile.

The diffractograms of composite materials TCli-20 and Tβ(19)-20 exhibit characteristic reflections of starting zeolites (Cli and β(19)) together with reflections originating from TiO_2 anatase phase (2θ = 25.3°, 37.9°, 48.1°) (JCPDS 89-4921). Loading of TiO_2 nanoparticles and preservation of zeolitic structure was confirmed by the XRPD analysis. Similar, UV-Vis DR spectra (data not showed) of composites confirmed loading of TiO_2 nanoparticles and that the preparation procedure did not affect significantly the

optical properties of TiO_2. In addition, FTIR spectra (data not showed) also confirmed that the zeolitic structure have not been affected by the TiO_2 loading.

The results of BPA degradation using P25 nanoparticles and composites TCli-20, Tβ(19)-20 and Tβ(180)-20 are shown in Figs 2 and 3. For comparison, the amount of used P25 in photocatalytic experiment was matched to 20 wt% of catalyst loading and denoted as (P25-20). Photolysis test (Fig. 2) revealed that the BPA remains stable in the absence of photocatalyst.

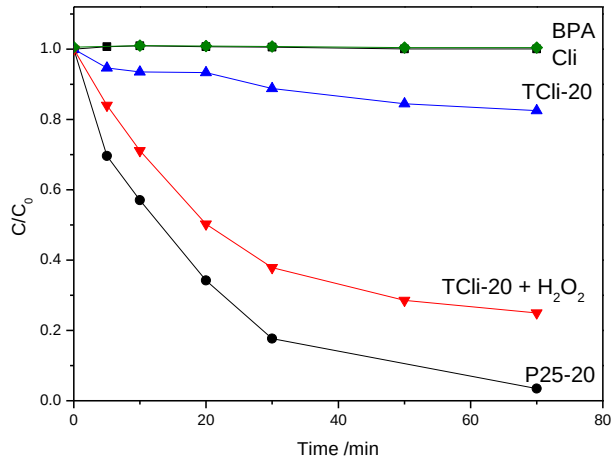

Figure 2. Degradation of BPA (C_0= 10 mgL^{-1}) using: Cli, P25-20, TCli-20 and TCli-20 with addition of 25 µl H_2O_2 (0 min – start of irradiation, C-concentration measured at 225 nm at different irradiation time).

The photocatalytic experiment conducted with TCli-20 (Fig. 2) revealed that after 70 minutes of irradiation only 17.5 % of BPA was degraded, whereas under the same conditions with addition of 25 µl H_2O_2 the degradation rate was significantly improved: 75.1 % of BPA was successfully degraded. Addition of H_2O_2 was beneficial to photocatalytical process as more $^{\bullet}OH$ radicals were formed. For the determination of reaction constant rates, the curves presented in Fig. 2 were used. The pseudo first order rate model was utilized and the rate constant values were determined as 0.003 min^{-1}, 0.027 min^{-1} and 0.050 min^{-1} for TCli-20, TCli-20 + H_2O_2 and P25-20, respectively.

In the experiments conducted with composites based on β zeolite (Fig. 3.) higher concentrations of BPA were used as the removal process is achieved through the adsorption and photocatalytic degradation. The results showed that during experiment in the dark using BPA concentration of 20 mgL^{-1} composite Tβ(19)-20 adsorbed 4.5 mgL^{-1}. In the case of composite Tβ(180)-20, BPA concentration C_0=50 mgL^{-1} was used because of the higher adsorption capacity of this zeolite compared to β(19) in order to achieve similar concentrations of BPA remained in aqueous solutions for photocatalytic tests. The composite Tβ(19)-20 successfully removed BPA after 120 minutes exposure to light, whereas P25-20 was slightly more efficient and completely eliminated BPA after 90 minutes (Fig. 3). However, in the case of Tβ(180)-20 prolonged irradiation is needed for complete elimination of BPA. The calculated pseudo first order constant rates were 0.004 min^{-1}, 0.019 min^{-1} and 0.023 min^{-1} for Tβ(180)-20, Tβ(19)-20 and P25, respectively. The degradation of BPA was followed by UV-Vis spectroscopy, and the UV-Vis spectra (data not shown) revealed that composite Tβ(19)-20 successfully achieved complete elimination of BPA and its potential by-products.

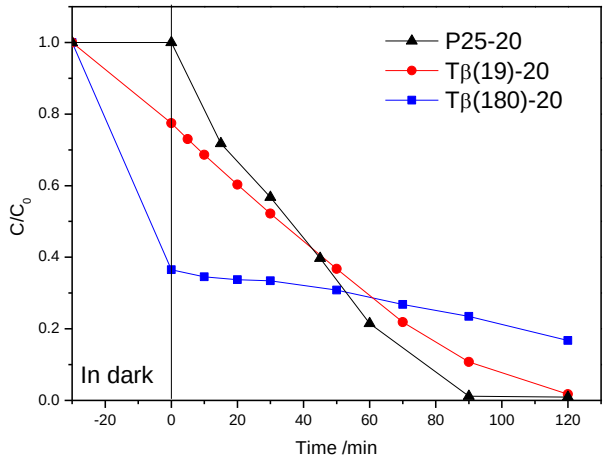

Figure 3. Removal of BPA using: C_0= 20 mgL^{-1} for P25-20 and Tβ(19)-20 and C_0= 50 mgL^{-1} for Tβ(180)-20 (0 min – start of irradiation, C-concentration measured at 225 nm at different irradiation time).

CONCLUSION

This study showed that successful photocatalytic degradation of BPA from aqueous solution can be achieved using low cost TCli-20 composite with addition of H_2O_2. Furthermore, complete removal of BPA was observed using composite material based on P25 and β zeolite with Si/Al = 19. The combined effect of adsorption by β zeolite and TiO_2 photocatalysis was favourable for complete removal of investigated contaminant.

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