Removal of methylene blue by activated glass foams with TiO_2 in dark and simulated solar light

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Abstract. Utilization of cheap, simple and efficient glass foams coated with various amounts of titanium dioxide (TiO_2), as an economic and environmentally friendly adsorbent and catalyst for the removal of methylene blue dye from aqueous solutions, has been investigated. The glass foam samples were obtained from 95% domestic glass wastes and 5% $CaCO_3$ wastes coming from marble industry. Further, the surface of glass foams is activated with TiO_2 obtained previously by hydrothermal method (crystallographic form anatase). The influence of TiO_2 content, stability and recyclability in time were evaluated. This study provides a view of a new type industrial material that can be used in as environment friendly material for building materials technology with high catalytic performance and reusability for the degradation of organic pollutants.

INTRODUCTION

Water discoloration has recently become an area of major scientific interest, as indicated by the multitude of related research reports. One of the biggest environmental problems is removing toxic organic compounds like methylene blue from water. Methylene blue is a thiazine (cationic) dye, which is most commonly used for coloring, but in high concentrations can be harmful on the environment as well as aquatic ecosystem [1,2]. Lately, several discoloration techniques have been reported but few have been accepted by industries, so there is a need to find alternative treatments that are effective and cost-effective in removing water dyes, such as surface adsorption and photocatalysis. A promising method used worldwide for water discoloration is adsorption with solid adsorbents, being one of the most effective methods of treating and removing organic contaminants from the liquid medium. Adsorption has advantages over other fast and technologically simple methods that involve low investment. This technique is particularly indicated for the removal of those pollutants that cannot readily be biodegraded [3]. Photocatalysis is an advanced oxidation process (AOP) that can be used for the removal of pollutants from aqueous media. The optimization of photodegradation processes is a highly studied subject of scientific research and aims to obtain materials with characteristic properties (crystallinity, specific surface area, interstitial or surface defects etc.), which gives the photocatalytic systems high efficiency, long operating time, the possibility of using on an industrial scale all of them obtained at a low price. The photocatalytic applications of TiO_2 in treatment the water containing dyes and heavy metals are relatively new and are based on combining the optical, chemical and electrical properties of the photocatalysts.

Titanium dioxide is a type of n semiconductor that absorbs photons in the UVA domain, which limits its application in solar power systems; however, TiO_2 photocatalytic systems with artificial UV sources have been applied for water decontamination, facilitated direct light absorption [4]. The use of TiO_2-coated foam glass in degradation processes of pollutants in wastewater is just beginning, but it is a way of ensuring the implementation of results in large-scale industrial processes. In particular, processes occurring in heterogeneous systems are extensively studied due to some advantages they offer, such as operating at ambient temperature and normal

pressure with easy recovery of the catalyst for re-use. Heterogeneous photocatalysis in the presence of semiconductor oxides is an oxidation process that is based on the irradiation of some semiconductors. Photocatalytic processes are reactions activate photochemical, characterized by active species, usually the OH radical [5], mechanism initiated by photon interaction (with some energy) with the chemical species present in the solution in the presence of a catalyst. Choosing the dyes to demonstrate the property of a self-cleaning material was a natural choice. The Japanese industrial standard JIS-R-1703-2:2007 uses methylene blue for evaluation of self-cleaning surfaces [6].

The use of foam glass as a support for TiO_2 is a viable and has great interest for photocatalysis. The production of glass foams is an effective way to recycle glass wastes, fly ashes and marble residues as foaming agent, allowing high incorporation percentages of these residues. The data on the effectiveness of the fading of different methylene blue stains are discussed. Next, a critical analysis is made of the different treatment methodologies and emerging technologies, with a note of their advantages and disadvantages.

EXPERIMENTAL

Catalysts preparation

Titanium dioxide (TiO_2) was prepared by hydrothermal method as follows: in 40 ml of distilled water was added 5 ml of acetic acid until it reached pH 4.5 and then 2 ml of titanium isopropoxide (Sigma Aldrich 99.9%) was added drop wise under continuous stirring. An opalescent solution was obtained which was stirred for another 30 min then was transferred in Teflon-lined autoclave that was sealed and introduced in the oven at 180° C for 5 hours. Afterward cooling was slowly done until room temperature. The precipitate obtained was separated from the supernatant by filtration and was washed several times with distilled water and ethyl alcohol to remove organic compounds, and then dried in an oven at 80 °C for 4 hours.

Foam glass preparation

In obtaining of foam glass we used industrial glass waste formed by glass micro spheres smaller than 36 μm in diameter. The glass powder from which the pills were carried out was obtained by grinding the glass waste in a ball mill. In order to obtain the foam glass pellet, we did so: 5 g waste glass powder (36 μm) with marble 5% (CaCO3 source) and ethylene glycol (6 drops) were mixed in agate mortar for 5 min for homogenization. Afterwards, the pastes were cast in molds of 25 mm (diameter) x 5 mm (thickness) and uniaxially pressed at 15 MPa to obtain white pellets. The samples were heat treated at 850 °C for 30 minutes with a temperature rise rate of 5°C/min. In this study we obtained 3 samples (S1, S2, S3) where S1 and S2 have same weight (1.35 g) and different amounts of TiO_2 (S1=0.02 g, S2=0.011 g). Sample 3 has 1.07 g and 0.016 g TiO_2 and was used in recyclability tests.

In order to study the effect of TiO_2 in photocatalytic processes, some of the cell glass pellets were immersed in 2% TiO_2 suspension in 1: 1 vol. water: ethylene glycol for 10 minutes and then dried in the oven at 80 °C. In order to increase the amount of TiO_2 deposition the process of impregnation was repeated twice. For a better fixation of the TiO_2 photocatalysts on surface of the foam glass, was applied heat treatment at 450 °C for 1 hour. Then weight of samples was measured before and after impregnation TiO_2 and amount of TiO_2 deposited was calculated.

During experiments each sample was immersed into 20 ml of methylene blue (MB) solution (5mg/L) in a beaker. The samples were kept in the dark for 6 h to achieve absorption/desorption equilibrium and then exposed to light irradiation for 120 min. Every 10 min 2 ml of MB solution was collected. The absorbamce of MB was determined at λ = 664 nm by using a UV-Vis Jaz spectrometer from Ocean Optics.

Characterization techniques

Structural characterization of powders has been carried out by X-ray diffraction (XRD) using a PANalyticalX′Pert Pro MPD-type diffractometer with Cu-Kα radiation (λCu = 1.54060 Å) and a 2θ-step of 0.016, from 20° to 80°.

Topographic surfaces were investigated with LEXT OLS4000 3D Laser Measuring Microscope designed for nanometer level imaging, 3D measurement and roughness measurement. Microscope magnification ranges from 108x – 17.280x and represent a new standard of surface roughness measuring tool and offers ideal capability to measure surface area texture. The crystal morphology and microstructure was observed using an Inspect S PANalytical model scanning electron microscopy (SEM). The elemental analysis was done with the EDX facility of the scanning electron microscope.

FT-IR spectrometer Vertex 70 (Bruker, Germany) in the range of 400-4000 cm^{-1} was employed to generate spectra with patterns that provide structural insights of samples analyzed. A powerful non-destructive method for material characterization is Raman Spectroscopy, which allows for the interrogation and identification of vibrational

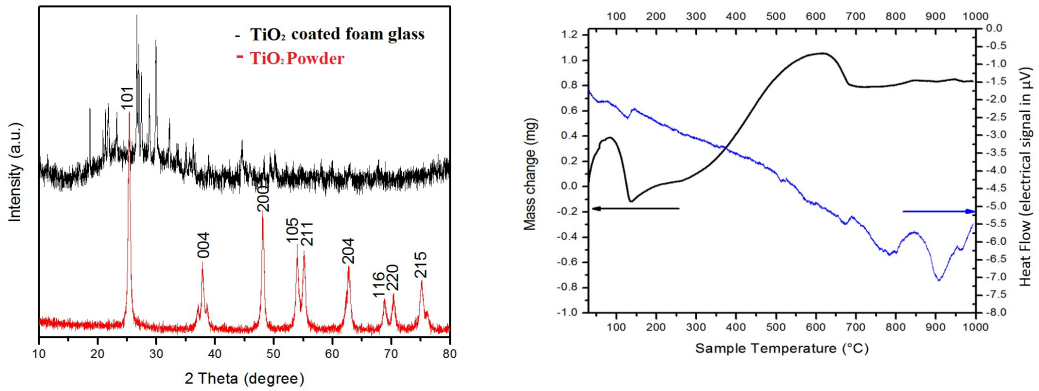
states of molecules. Nanonics Imaging (Israel) - MultiProbe Imaging - MultiView 1000™ (SPM) with 532 nm Laser was used in order to identify the vibrational states of molecules.

The photocatalytic experiments of all samples were performed under a solar simulator Sol2A 94042A from Oriel Instruments Newport Corporation with ultraviolet and visible fraction of simulated solar radiation measured with a UVA/UVB radiation detector (PCE-UV34) indicating an irradiance power of 1.12 mW cm^{-2} in UV and 847 W m^{-2} in VIS spectrum, irradiance measured with solar analyzer SOLAR-4000 Sensor provided by Beha-Amprobe.

RESULTS

Structural and Thermogravimetric Characterization

Crystalline phases for both the TiO_2 powder and foam glass mixture were determined by using X-ray diffraction (XRD). By comparing differences in XRD patterns, characterization of crystalline phases can be made and it can also provide useful information about microstructure of materials. TiO_2 anatase structure type was confirmed by XRD analysis represented in Fig. 1 (a). TG analysis (Fig. 1 (b)) illustrates the transformations that occur in the material under heat treatment with the heat flow given by machine.



(a) (b)

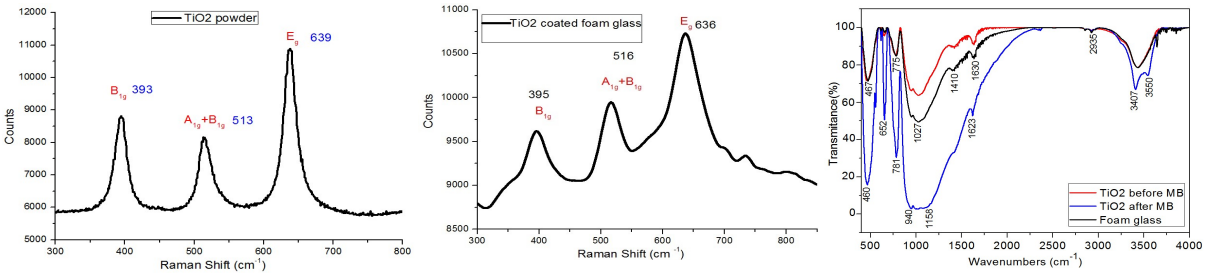
FIGURE 1. (a) XRD spectra of TiO_2 powder obtained by hydrothermal method (RED) and TiO_2 coated foam glass (black). (b) Thermogravimetric analysis of TiO_2 coated foam glass (TGA BLACK) with the heat flow given by machine (BLUE).

Thermogravimetric analysis shows mass losses and phase transformations around 150°C and 750°C. By means of this, the presence of three zones of mass loss can be observed: the first around 150 °C, attributed to the loss of the adsorbed water, the second at 300–550 °C, related to the decomposition of organic matter, and the third between 640 and 750 °C, attributed to the decomposition of $CaCO_3$ but it is confirmed that amounts of $CaCO_3$ still remain in sample after this temperature [7].

Raman and FT-IR Characterization

Raman Spectroscopy provided information about the molecular structure in order to identify substances based on characteristic "fingerprinting" as well as monitoring changes in molecular bond structure like state changes, formation of product or degree of crystallinity. Raman spectroscopy can identify naturally occurring crystalline phases such as anatase, rutile and brookite in TiO_2. Raman spectra of anatase have been observed in TiO_2 powder and foam glass coated with TiO_2 (Fig. 2 (a)). The FT-IR spectra before and after adsorption of methylene blue (MB) on the surface of foam glass raw and activated with TiO_2 are shown in Fig. 2 (b).

Both samples show the same spectral features in Raman spectra. According to literature the temperature of anatase to rutile phase transformation is about 900 °C while TiO_2 is linked to a substrate [8]. Heating the samples at 850 °C the anatase structure didn't change maybe because of high connection between foam glass and TiO_2 which inhibit the anatase-to-rutile phase transition. It was observed in recent developments that TiO_2 can be found in anatase form at high temperatures [9]. In Fig. 2 (c) the FT-IR Spectra of foam glass sample coated with TiO_2 before and after photocatalysis compared with uncoated foam glass are presented.



(a) (b) (c)

FIGURE 2. (a) Raman spectra of TiO_2 powder and (b) TiO_2 decorated foam glass and (c) FT-IR Spectra of foam glass sample coated with TiO_2 before and after photocatalysis compared with uncoated foam glass

The anatase phase of TiO_2 has six Raman active modes (A1g + 2B1g + 3Eg). All three measureable Raman vibration modes (B_{1g}, A_{1g}, and E_g) were active. The other E_g modes are below the measurement capabilities of our system. This is in agreement with other Raman analysis for the anatase phase of TiO_2 [10]. The line width of all of the three modes from TiO_2 coated glass increases with thermal treatment. The shape of the Raman peaks can change because of a pressure effect on the grains, induced by the surrounding grains or by the surface tension, which has been often invoked in similar cases. In our case, the thermal treatments are performed in air and the non-stoichiometry is expected to be negligible, as G. D. Venkatasubbu et all have proven in theirs study [11]. In addition, Raman and XRD measurements suggest that only the anatase phase is present.

The characteristic absorption peaks of the FT-IR analysis is shows several typical absorbance peaks ranging from wavelength 4000 to 400 cm^{-1}. Thus peaks to 3407 and 3550 cm^{-1} can be assigned to the O–H stretching vibration mode of hydroxyl functional groups [12]. The band observed at 2935 cm^{-1} suggests the presence of C–H stretching vibrations derived from the ethylene glycol used to obtain foam glass pellets. The peaks at 1623 and 1630 cm^{-1} represents C=O stretching vibrations of carbonyl compounds absorbed on the pellet surface [13]. The band at 1410 cm^{-1} represents the bending vibrations of C-H. The bands from 450-1200 cm^{-1} show a mixture of bonds vibration of inorganic and organic functional groups from materials studied. The spectra show an intense and broad band at between 900 -1200 cm^{-1} related to the stretching vibrations of M-O groups, with a shoulder appeared at 940 cm^{-1}, which can be assigned to external Si-OH groups, while the bands around 460 cm^{-1} are due to M-O-M bending vibrations [14]. The band at 652 cm^{-1} is assigned to couple M-O out-of-plane vibrations. The presence of oxide mixtures is confirmed by a sharp band at 781 cm^{-1} [15]. The vibration bands of the =N $(CH_3)_2$ (1623–1630 cm^{-1}) and C-S-C (625-615, 1158 cm^{-1}) functional groups are characteristic of the presence of MB monomers in the studied samples. These peaks were shifted to lower-frequency region relative to free MB molecules. It was concluded that there is a significant influence of intermolecular interactions on the listed functional groups, providing the formation of MB hydrates [16]. The absorption peaks for sample "TiO_2 after MB" indicates a slight shift of the spectrum to lower wavelengths and an increased the absorbance intensity at these wavelengths, probably partially responsible for the dye adsorption. Similarly, the intensity of peaks for sample "TiO_2 before MB" was decreased compared to foam glass sample.

Morphological Characterization

SEM images of TiO_2 coated and uncoated foam glass are represented in Fig. 3 (a). TiO_2 nanoparticles deposited on foam glass sample were determined with EDX Spectroscopy. The shape of TiO_2 nanoparticles is undefined form. Profilometry was used in the evaluation of surfaces (area, surface roughness, area surface and volume) of all samples (Fig. 3 (b)). The visualization of recorded image generates an image of the surface height 3D using LEXT software, by setting the upper and lower limits on the size of the features that is characterized. The camera magnification was 21.6 X and ocular used was 10X.

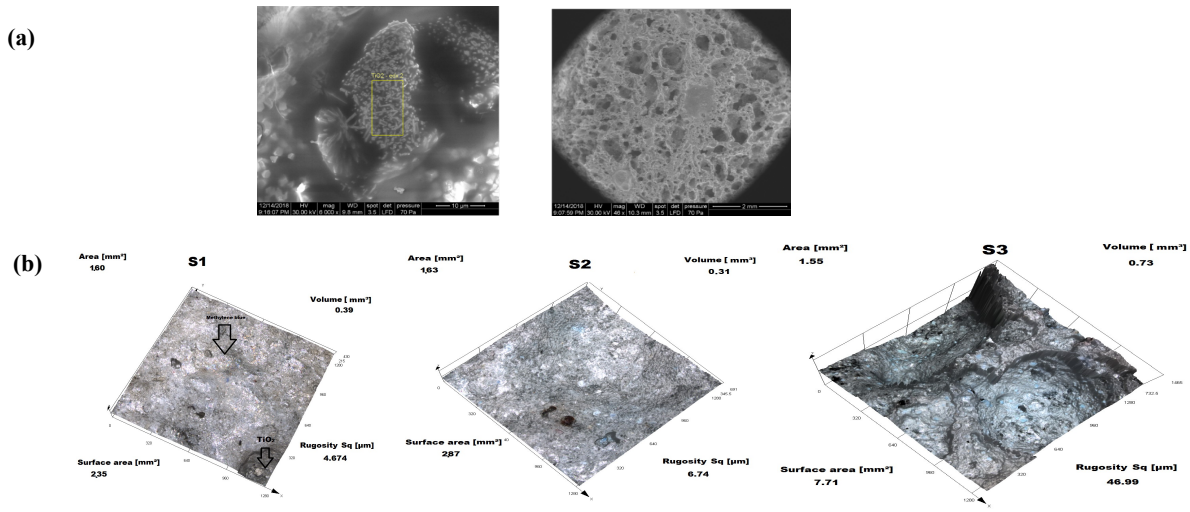


FIGURE 3. (a) SEM micrographs recorded of TiO_2 coated foam glass and uncoated foam glass (b) 3D Images of all samples

It can be observed that S1 and S2 are similar in surface characteristics while S3 has 10 times higher rugosity which can affect the adsorption and photocatalysis activity. The Methylene blue and TiO_2 can be observed on all surfaces.

Photocatalytic activity

When light irradiates the foam glass surface decorated with TiO_2 nanostructures, an electron is released from its surface and reacts with the oxygen and water in the atmosphere to form superoxides and hydroxyls. In contact with methylene blue in water, superoxides and hydroxyls convert the organic into H_2O and CO_2. The photocatalytic activity of the foam glass coated with TiO_2 was evaluated by determining the photodegradation efficiency of the dye. The steps taken to calculate the photodegradation efficiencies were:

- setting the absorption maxima by plotting the absorption spectra on the 350-1000 nm range;
- the formula used to determine the efficiency (η %) of dye degradation was: $\eta = \frac{A_0 - A}{A_0} \times 100$, where A_0 is the absorbance of the dye solutions measured before lighting and A is the absorbance of the dye solutions after 120 min of illumination.

In order to evaluate the weight of TiO_2 influence in photocatalysis samples S1 and S2 were exposed in same conditions to solar simulator in MB cuvette. The photocatalytic activity of the S1 and S2 is measured by photocatalytic decomposition of an organic dye (methylene blue). Samples S1 and S2 were washed before use with ethanol in order to clean the surface from any contaminants. The normalized absorbance graphs comparison between samples with different amounts of TiO_2 is shown in Fig. 4 (a). It can be observed that with increase of TiO_2 amount the adsorption increased which increased photocatalysis activity. Removal of methylene blue increased with 9% with increasing TiO_2 from 0.01 mg to 0.02 mg.

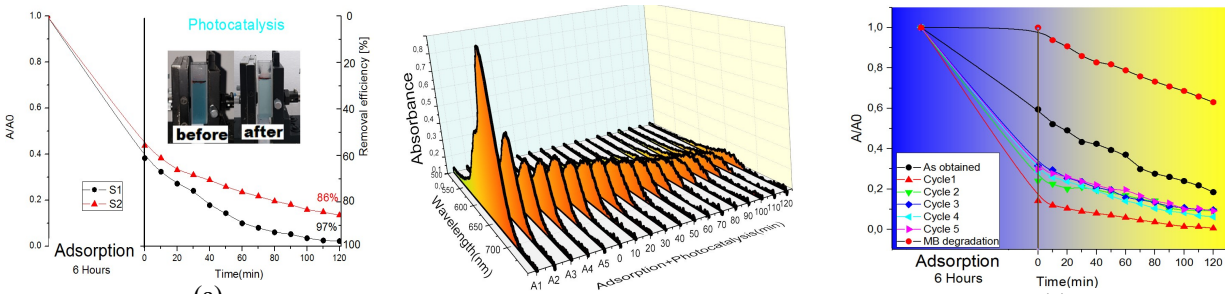


FIGURE 4. (a) Methylene blue removal process for S1 and S2. (b) Absorption spectra of methylene blue solution for different irradiation times where S3 was used as photocatalyst. (c) Recyclability tests for S3.

In order to evaluate the importance of previous cleaning process the sample S3 was exposed directly to experiment without any previous ethanol cleaning named Fig. 4 (c) as obtained sample S3. After cleaning with ethanol the as obtained sample photocatalytic efficiency was improved with 5%. The removal of methylene blue was 99%. One of the unique aspects of TiO_2 is that there are actually two distinct photo-induced phenomena: the first is the well-known photocatalytic phenomenon that leads to the decomposition of organics, and the second called "superhydrophilicity". Although there are intrinsically different processes in fact they must take place simultaneously on the same TiO_2 surface. Depending on composition and processing, the surface may have more photocatalytic character and less superhydrophilic character or reversed [17]. This study focuses on the enhancement of the effectiveness of the photocatalytic process by increasing of roughness on the exterior foam glass surface. The enhanced adsorption and photocatalysis would translate to an increased in the mass transfer of methylene blue contaminants to the catalyst surface, improving the efficiency of photocatalysis. This can explain the small difference between photocatalysis activity of samples.

CONCLUSION

In conclusion, we have obtained activated glass foam samples coated with various amounts of titanium dioxide (TiO_2) catalyst used for the removal of methylene blue (MB) dye from aqueous solutions. The activated glass foam samples showed a high activity for methylene blue removal. The MB removal reached more than 90% in 2 hours for 20 ml aqueous solution of MB with concentration of 5mg L^{-1} under simulated solar radiation.

The structural properties of the obtained samples were characterized by: X-ray diffraction (XRD), Thermal analysis (TG/DTA), Raman and FT-IR spectroscopy. The surface morphology of the foam glass pellets was studied using Scanning Electron Microscopy (SEM) and 3D Profilometry. Reusability of the catalysts was examined in order to establish their stability and recyclability. This study provides a clear view of new type industrial material which can be used in as environment friendly material for building materials technology with high catalytic performance and reusability for the degradation of organic pollutants.

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