



Synthesis and characterization of nanoparticles and composites as bactericides



Laleh R. Kalankesh^a, Susana Rodríguez-Couto^b, Mohammad Ali Zazouli^{c,*},
Yousef Dadban Shahamat^d, Ramazan Ali Dianati^c, Mahdieh Arghiani^{c,*}

^a Department of Environmental Health Science, Health Sciences Research Center, School of Public Health, Mazandaran University of Medical Sciences, Sari, Iran

^b IKERBASQUE, Basque Foundation for Science, Maria Diaz de Haro 3, Bilbao 48013, Spain

^c Department of Environmental Health Engineering, Health Sciences Research Center, Faculty of Health, Mazandaran University of Medical Sciences, Sari, Iran

^d Environmental Health Research Center, Department of Environmental Health Engineering, Faculty of Health, Golestan University of Medical Sciences, Gorgan, Iran

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ABSTRACT

In the present study, SiO₂-TiO₂ hybrid nanomaterial and zeolite-TiO₂ (Z-TiO₂) composites were synthesized by the sol-gel method. Then, the antibacterial activity of the above-mentioned synthesized materials, SiO₂ and zeolite (Z) was investigated by the disk diffusion method using *Echerichia coli* and *Enterobacter aerogenes* as test microorganisms. All the materials showed antibacterial activity against *E. coli* with 7.2, 10.7, 3.5 and 8.2 mm of inhibition zone for SiO₂-TiO₂ hybrid nanomaterial, SiO₂, zeolite and Z-TiO₂ composite, respectively. However, none of them showed antibacterial activity against *E. aerogenes*. The obtained results pointed out that these natural-based materials (i.e. Z, SiO₂, Z-TiO₂ and SiO₂-TiO₂), known to be noncarcinogenic and nontoxic, can be used as disinfectants against *E. coli* (an important indicator of the bacteriological quality of water) as safe and eco-friendly alternatives to chlorine.

1. Introduction

Over the last decade, statistical studies have shown that diseases transmitted from contaminated water or human excretion cause most of the mortality around the world (Wang et al., 2015; Li et al., 2017; Zazouli and Kalankesh, 2017; Zazouli and Kalankesh, 2018). According to epidemiological studies, 80% of the reported diseases are related to waterborne pathogenic microorganisms like *Echerichia coli* and *Enterobacter aerogenes* (Chandra et al., 2017). These bacteria, which are indicators of water potability (Edberg et al., 2000a, 2000b), are estimated to cause up to 40–80% of infant mortality each year worldwide (Kim et al., 2009). Water disinfection reliability, safety and efficiency have become an increasingly challenge issue throughout the world (Collivignarelli et al., 2017). Traditional water disinfection methods such as advanced oxidation processes, ultraviolet radiation (Vaferi et al., 2014), ozonation (Lee et al., 2014; Szymanska et al., 2014), membrane bioreactors (Zanetti et al., 2010; Chen et al., 2012), hybrid treatment systems (Abdel-Shafy et al., 2014) and chlorination require expensive chemicals or costly equipment and generate unwanted by-products (Li and Zhang, 2013). Nowadays, chlorination is widely used for disinfection of potable water in most countries. However, it is ineffective against highly resistant bacteria and also forms some

carcinogenic byproducts (Zazouli and Kalankesh, 2017). Therefore, the development of efficient and environmentally friendly disinfection strategies is an urgent need. Accordingly, some nanomaterials have been applied as antimicrobial agents to consisting home refinement systems and consumer producers (Padmavathy, 2008, Lemire et al., 2013a, 2013b). Recent studies have shown that several nanoparticles such as those made of zinc oxide (ZnO₂), silver (Ag) and titanium dioxide (TiO₂) display antimicrobial properties without strong oxidation ability (Daou et al., 2017, Shuai, Shuai et al., 2018). Research showed that the application of inorganic nanoparticles and their surface modifications achieved good antimicrobial activity (Camporotondi et al., 2013). Titanium dioxide is the most commonly photocatalytic antibacterial nanoparticle used since it kills both Gram-negative and Gram-positive bacteria (Camporotondi et al., 2013). Silica nanoparticles are one of the most common natural minerals having a high specific surface area and porosity together with antibacterial activity (Yu et al., 2017; Priyadarsini et al., 2018). The nanohybrid material SiO₂-TiO₂ with different surface characteristics is conducive to different antibacterial activities (Besinis et al., 2014). Among various materials used as a support, zeolites have been found to perform better than TiO₂ due to their unique crystal structure and uniform nanoscale pores and channels which give them a large surface area and induce the synergistic

* Corresponding authors.

E-mail addresses: zazoli49@yahoo.com, mzazouli@mazums.ac.ir (M.A. Zazouli), m.arghiani1985@gmail.com (M. Arghiani).

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adsorption of organic matter (ALothman, 2012). Nowadays, a variety of nanomaterials with antibacterial activities has been developed among which SiO₂ presents higher thermal and chemical stability, higher surface area and better biocompatibility and, thus, it is extremely used as an antibiotic drug delivery (Haidary et al., 2012). Accordingly, SiO₂ was selected to perform the present study. In recent years, many authors have used TiO₂ or mixed oxides such as Ag/TiO₂-SiO₂ against hospital acquired infections. However, there is no report regarding the comparison of the application of synthesized TiO₂-SiO₂ hybrid nanomaterial and Z-TiO₂ composite with other natural materials such as zeolite and SiO₂ as an antibacterial agent (Chien et al., 2012; Erdural et al., 2014). Consequently, in the present work natural titanium nanocomposites were synthesized in order to develop an efficient and environmentally friendly approach to disinfect drinking water. Also, the antibacterial properties of the synthesized nanoparticles against *E. coli* and *E. aerogenes* were assessed.

2. Materials and methods

2.1. Chemicals and standards

All the analytical standards were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). Zeolite (Z) was supplied by Zeolyst International (CBV 100) with a SiO₂/Al₂O₃ molar ratio of 6/1; nominal cation in sodium form (Na₂O weight (%): 2.01). The unit cell size of Z was 24.65 Å and the surface area was 900 m²/g. Titanium (IV) isopropoxide (TTIP, 99.99%, Aldrich, Germany), titanium dioxide (TiO₂) and silica dioxide (SiO₂) were provided by Sigma-Aldrich Co. (St. Louis, MO, USA.) The Physicochemical characteristics of the commercial TiO₂ and SiO₂ are indicated in Table 1. All the microbiological reagents were obtained from Millipore India Ltd. (Mumbai, India). Barium chloride (Fluka, Buchs, Switzerland) and sulfuric acid (Fisher Scientific, Waltham, MA, USA) were used for McFarland standard preparation. All aqueous solutions were prepared using double distilled water (DDW).

2.2. Microorganisms

The Gram-negative bacterium *Echerichia coli* and *Enterobacter aerogenes* were isolated from polluted water taken from a contaminated shallow aquifer water located in the nearby of the Mazandaran University of Medical Science.

2.2.1. Isolation and identification of coliform bacteria

Total coliforms and faecal coliforms were determined by the Most Probable Number (MPN) method (Association, Association et al., 1915). Coliform bacteria were isolated by taking a loopful of positive BGB (Brilliant Green lactose-bile Broth) medium tubes (Oxoid), streaking them onto MacConkey agar Petri plates and incubated them at 37 °C for 18–24 h. Primary isolates were identified by Barrow and Feltham methods and then followed by IMViC tests for differentiation (Barrow and Feltham, 2003).

2.2.2. Isolation and identification of *E. coli*

A loopful of positive *E. coli* medium tubes (Oxoid) was taken from the MacConkey agar Petri plates and, incubated at 37 °C. Primary *E. coli* isolates from MacConkey agar (pink colonies) were examined by using Eosin Methylene Blue Agar plate (EMB) (Oxoid) as a selective medium

Table 1
Physicochemical characteristics of the commercial TiO₂ and SiO₂ nanoparticles.

Appearance	Purity%	Special surface (m ² /g)	Size (nm)	Type of nano particle
White powder	99	10–45	20	TiO ₂
White powder	99	600	10	SiO ₂

for *E. coli*. Colonies showing a metallic green sheen were recorded as positive *E. coli*. Then metallic green sheen colonies were cultured into Colic Brilliance *E. coli* coliform selective medium (Oxoid) for further confirmation. Blue or violet colonies were recorded as positive *E. coli*.

2.3. Synthesis of Z-TiO₂ composites

The Z-TiO₂ catalysts were prepared via the sol-gel method (Cano-Casanova et al., 2018). Titanium tetraisopropoxide (TTIP, Aldrich, 99.99%) was used to prepare the transparent TiO₂ sol at room temperature as follows: firstly, 5 g of Z was added to 30 mL of ethanol (in order to control the sol-gel reactions hydrolysis and condensation) and stirred for 3 h to get a precursor solution. Then, a mixture of 0.26 mL of DDW, 3.4 mL of glacial acetic acid and 5 mL of TTIP was dropped into the precursor solution at a speed of one drop per second under high rotating speed. The obtained solution was stirred for some minutes and then 30 mL of DDW was added dropwise. The pH was adjusted to 2.5 by using 1 M nitric acid solution. The obtained suspension was kept under continuous stirring for 1 h. The composite sol was filled at room temperature and then dried at 60 °C overnight. Finally, the dried sample was calcined at 450 °C for 3 h in a muffle furnace (Ratiu et al., 2011).

2.4. Synthesis of the TiO₂-SiO₂ nanoparticle composites

The preparation of the TiO₂-SiO₂ nanoparticle composites by the sol-gel method was carried out in several steps. The hybrid precursor (sol) was prepared by mixing TiO₂ and SiO₂ nanoparticles (20% wt.) (1:3 v/v) in 10 mL of ethanol for 2 h at room temperature. Next, the sol solution was maintained for 4 h at 100 °C in an oil bath. Then, 1 mL of citric acid and ethylene glycol were added to the obtained sol solution as crosslinking agents. The hybrid precursor precipitated forming the gel. The final gel solution was left undisturbed for 24 h. Finally, the gel solution was heated at 120 °C for 1 h and then calcined at 500 °C for 4 h. Studies have shown that the proper molar ratio of mixture of Titanium silica gain additional stability and according studies have been done TiO₂/SiO₂ have a higher stability in the 3/1 ration according their molecular weight.

(Balachandran et al., 2010, Malakootian et al., 2013a, 2013b, Mansouri et al., 2015).

2.5. Antimicrobial activity

The disc diffusion method was used to screen the antibacterial activity of the synthesized nanoparticle composites against the isolated Gram-negative *E. coli* and *E. aerogenes* bacterias as test microorganisms. For this, Mueller-Hinton agar (MHA) plates were prepared by pouring 5 mL of MHA medium supplemented with 2% NaCl (v/v) into sterile Petri plates (Wu et al., 2017). After solidification and cooling down, the plates were swabbed with 1 mL of bacterial cultures, previously cultured in 10 mL centrifuge tube (Falcon) at 37 °C and 100 rpm for 12 h, with a turbidity of 0.5 in the McFarland scale. Assay-discs (MastDiagnosics, UK) impregnated with 0.1 g of the nanoparticle composites were loaded on the surface of the agar plates and the compound was allowed to diffuse (Clinical and Institute, 2009). Inhibition zones (in mm) were measured after incubation at 37 °C for 24 h.

2.6. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

Scanning electron microscopy (SEM) was used to determine the surface morphology of Zeolite and Z-TiO₂ and transmission electron microscopy (TEM) to determine the nanoparticle size of the TiO₂-SiO₂ hybrid composite, SiO₂ and TiO₂. SEM (Hitachi Model S3000 N VPSEM) images were taken at 100 x magnification at an accelerated voltage beam strength of 1 kV. TEM equipment has been used to observe nanomaterials with size smaller than 100 nm and obtaining quantitative

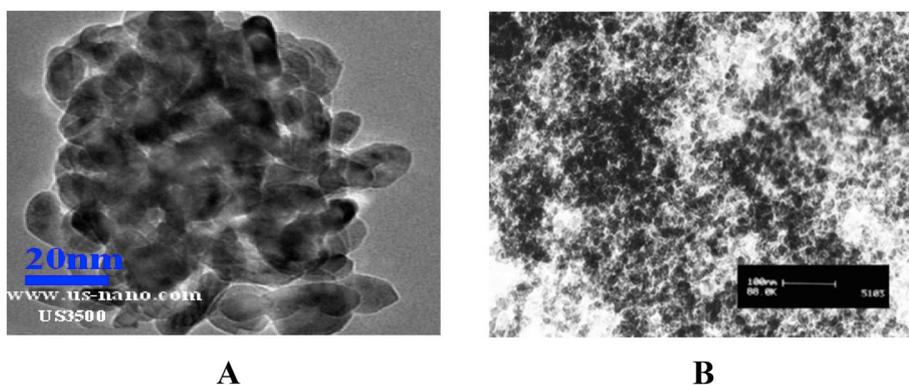


Fig. 1. Transmission electron microscopy (TEM) photographs of TiO_2 (A) and SiO_2 (B) nanoparticles (Nano Pars Nima).

results (Kling et al., 2008; Schamm et al., 2008). Thus, TEM (JEOL JEM2100 microscope operating at 200 Kv) was used to observe the nanohybrid TiO_2 - SiO_2 samples.

3. Results and discussion

3.1. Characteristics of the commercial and synthesized nanoparticle composites

3.1.1. Commercial TiO_2 and SiO_2 nanoparticles

In Fig. 1, TEM photographs of the commercial TiO_2 (Fig. 1A) and SiO_2 (Fig. 1B) nanoparticles, which are used to synthesize the composites are shown. As can be seen, TiO_2 anatase crystal has a tetragonal bipyramidal form or a truncated pyramid (or bipyramid) with square facets (Fig. 1A) and the SiO_2 nanoparticles showed the typical ball-like geometry of silica, which consists of spherical particles with poor agglomeration (Fig. 1B). In addition, the crystal structure of each nanoparticle of TiO_2 and SiO_2 was characterized by the grazing incidence X-ray diffractometer between 20 and 70 Bragg angles (the following pictures were received from “Nano Pars Nima “Company) (Fig. 2).

3.1.2. Z- TiO_2 composites

The surface morphology of the parent zeolite and the Z- TiO_2 nanocomposite at different magnifications are shown in Figs. 3 and, respectively. As it can be observed, the morphology of the nanocomposite differs significantly from the morphology of the parent zeolite. Thus, after modification the TiO_2 particles were clearly visible as white colored regions on the surface of the zeolite matrix. The structure of the natural sunlight had a good thermal stabilization and revealed that most TiO_2 particles were distributed on the surface of the natural zeolite while in the synthesized Z- TiO_2 nanocomposite the TiO_2 particles were encapsulated into the cavities of the natural zeolite. This indicated that no strong chemical interactions took place between the

TiO_2 and the zeolite (Fig. 4). The surface morphology of Z- TiO_2 indicated that the TiO_2 nanoparticles were homogeneously dispersed within the zeolite framework (Jansson et al., 2017). According to the SEM images (Fig. 3), the unmodified zeolite has a cubic shape. In addition, it was observed that the surface of the zeolite was smooth with well-defined edges and after coating with TiO_2 the roughness of the surface increased remarkably (Latha and Karuthapandian, 2017). It could also be observed that the TiO_2 coating was relatively uniform with no apparent sites of uncoated zeolite. In addition, in Fig. 4 pore openings and cavities resulting in an increased specific surface area of the composite, thus providing higher adsorption sites for contaminant adsorption, were shown. This result was consistent with the results found by other researchers (Zhao et al., 2010; Liu et al., 2014; Chang et al., 2015)

3.2. SiO_2 - TiO_2 nano particle composites

In Fig. 3 the SEM images of the SiO_2 - TiO_2 nanocomposite are shown. The commercial TiO_2 presented a glassy and smooth surface with cracks while, the surface roughness and porosity was increased by adding SiO_2 (Fig. 6) (Dang et al., 2010). The SiO_2 - TiO_2 nanoparticle composites had a spherical shape with approximately 50 nm in diameter as shown in Fig. 5. The results suggested that, the formation of larger SiO_2 - TiO_2 nanoparticles (50 nm) in comparison with the commercial TiO_2 (20 nm) and SiO_2 (10 nm), was due to the agglomeration and sintering during the calcinating process (Hanaor et al., 2012). According to Fig. 1 silica nanoparticles with a honeycomb structure can be hybridized with TiO_2 forming a uniform material with improved surface structure characteristics of TiO_2 nanoparticles. Also, as seen from Fig. 1 the commercial TiO_2 had a glassy and smooth surface with cracks (Fig. 1A) while the commercial SiO_2 had a roughness surface with high porosity (Fig. 1B).

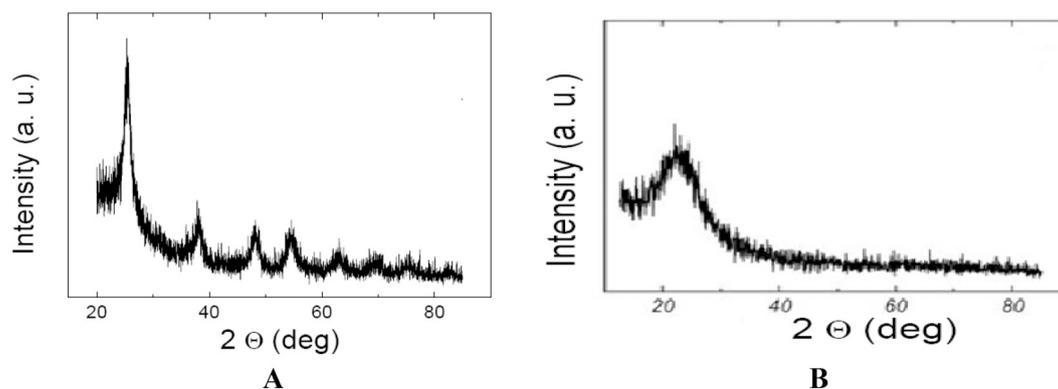


Fig. 2. X-ray diffraction patterns of TiO_2 (A) and SiO_2 (B) nanoparticles (Nano Pars Nima).

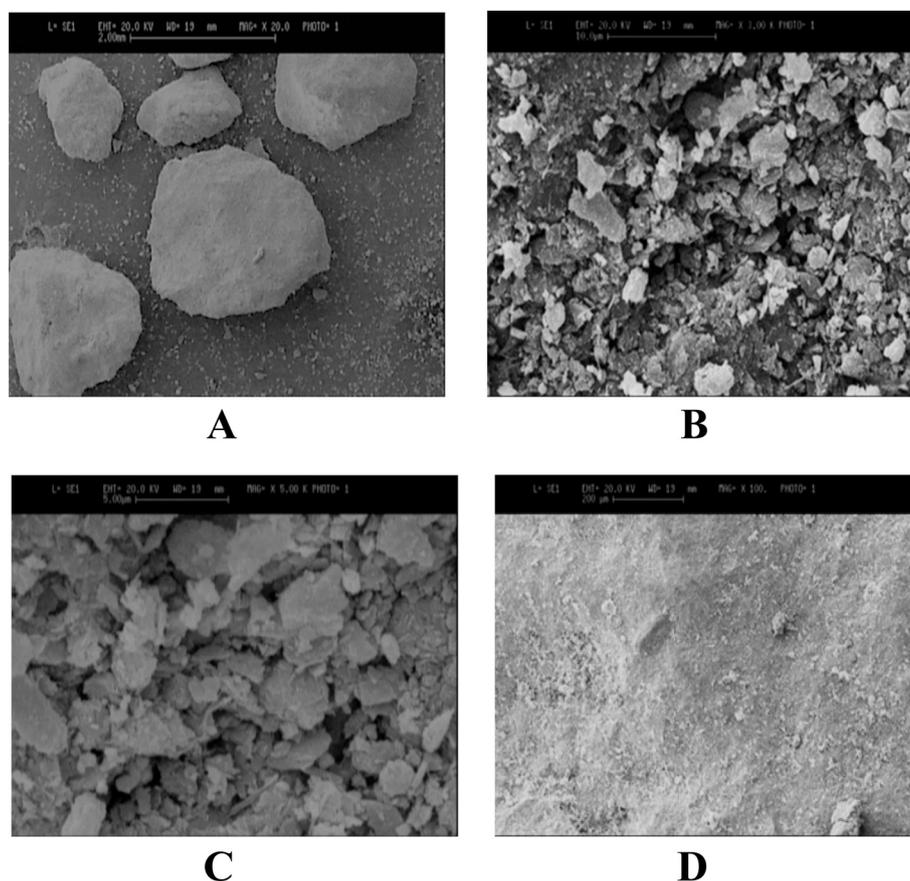


Fig. 3. SEM image of parent zeolite (a) $2,0\times$ magnification, scale bars: $2,00\text{ nm}$; (b) $3,00\times$ magnification, scale bars: $10,0\text{ }\mu\text{m}$; (c) $5,00\times$ magnification, scale bars: $5,00\text{ }\mu\text{m}$; (d) $1,00\times$ magnification, scale bars: $2,00\text{ }\mu\text{m}$.

3.3. Antimicrobial activity tests

The antibacterial activity of the synthesized Z-TiO₂ and SiO₂-TiO₂ nanoparticle composites was tested by the Kirby-Bauer diffusion method (Hudzicki, 2009) using the Gram-negative bacterium *E. coli* and *E. aerogenes* as test microorganisms. From the obtained results, it can be clearly observed (Fig. 7) that the commercial SiO₂, the zeolite and the synthesized SiO₂-TiO₂ and Z-TiO₂ showed antibacterial activity against the Gram-negative bacterium *E. coli*. The average inhibition zones against *E. coli* were 10.7, 8.2, 7.2 and 3.5 mm for SiO₂, Z-TiO₂, SiO₂-TiO₂ and zeolite, respectively (Fig. 7A). However, none of the examined nanoparticles had antibacterial activity against the Gram-positive bacterium *E. aerogenes* (Fig. 7B).

According to the obtained results of the antibacterial activity, the antibacterial mechanism of the developed nanoparticles was supposed to be as follows: The inactivation of the bacteria occurred over their exterior cell wall which is composed of lipopolysaccharides, phospholipids and transmembrane proteins. Based on the membrane properties of the bacteria, the highest antibacterial efficiency of the SiO₂ nanoparticle was related to the interaction with the lipopolysaccharides through a hydrogen bond formation between the saccharides and the hydroxyl groups present on the silica surface (Hudzicki, 2009). Although several studies were carried out on the application of nanoparticles against Gram-positive and Gram-negative bacteria, their antibacterial mechanisms have not been completely elucidated (Aprioku, 2013). Furthermore, the same types of nanoparticles often present contrasting effects on different bacteria. So, in spite of several studies reported that TiO₂ nanoparticles alone had very good antibacterial performance (Gupta et al., 2013; Verdier et al., 2014; Arora et al., 2015), so in this study, try to focus on the investigating hybrid synthesized nano composite of TiO₂. The obtained results in the present

study showed that the bacterial inactivation of SiO₂-TiO₂ (7.2 mm) and Z-TiO₂ (8.2 mm) were smaller than that of SiO₂ (10.7 mm). In addition, the antibacterial activity against bacteria improved by increasing the surface area of the nanocomposites (Abdal Dayem et al., 2017). The surface area and surface roughness of SiO₂-TiO₂ nanocomposites are strongly related to their surface free energy. The surface free energy is an important factor for free radical generation rate, bacterial adhesion and inactivation (Xiao et al., 2018). The surface area of the nanoparticle decreases by increasing the nanoparticle size (Malakootian et al., 2013a, 2013b). On the other hand, When the nanoparticle size increases, its surface irregularities or pores could be occupied decreasing the surface area. In the present study, the size of SiO₂-TiO₂ synthesized nano composites increased and effect on the surface properties of the composite so, their antibacterial activity would partly decreased in comparison with SiO₂ and Z-TiO₂ nano material (Zhang, Zhang et al., 2015). It was reported that the antimicrobial mechanism of nanoparticles follows three models: oxidative stress induction (Gurunathan et al., 2012), metal ion release (Nagy et al., 2011) and non-oxidative mechanisms (Leung et al., 2014). Therefore, another important factor on the inactivation of bacteria were the reactive oxygen species (ROS) which were generated over the TiO₂ surface by the oxidative stress induction mechanism and reacted readily with the cell wall of the adhered bacteria (Wang et al., 2017). Also, the role of the surface structure-bacterial adhesion relationship should not be deniable (Rtimi et al., 2017). Most researchers reported that suspended bacteria in water were more susceptible to the attack of short-lived ROS so, the inactivation rate of adhered bacteria are much more difficult than those of suspended bacteria (Zhou et al., 2015; Aboubakr et al., 2016; Zhou et al., 2016; Wang et al., 2018). *E. coli* and *E. aerogenes* are suspended bacteria in water (Edberg et al., 2000a, 2000b) and our results confirmed that SiO₂-TiO₂ had antibacterial effect against a Gram-positive

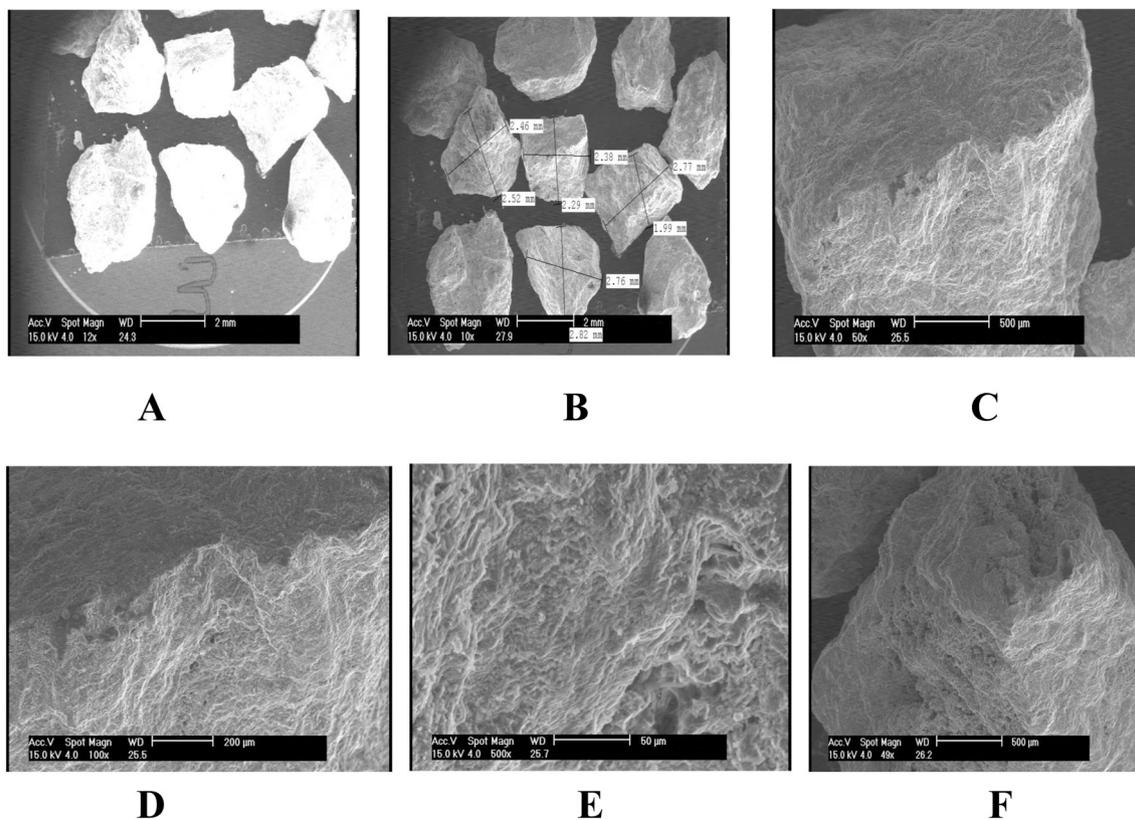
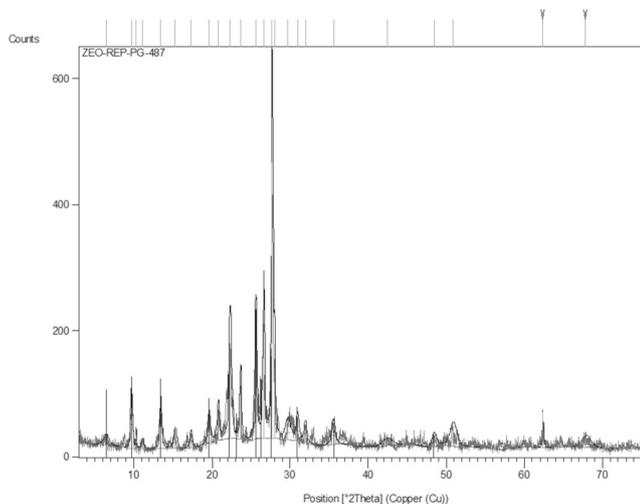


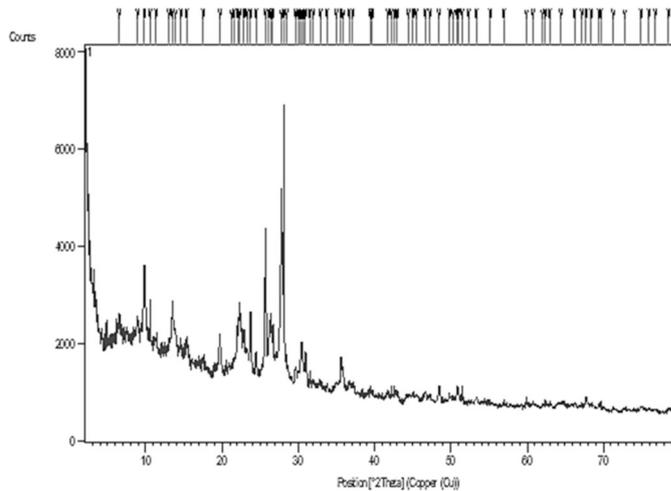
Fig. 4. SEM image of the synthesized Z-TiO₂ composites (a) 12× magnification, scale bars: 2 mm; (b) 10× magnification, scale bars: 2 mm; (c) 5,0× magnification, scale bars: 5,00 μm; (d) 1,00× magnification, scale bars: 2,00 μm; (e) 5,00× magnification, scale bars: 5 μm; (f) 49× magnification, scale bars: 5,00 μm.

bacterium (i.e. *E. coli*). Among various supports for TiO₂, zeolites showed to be more favorable (Ko, 2008) because their unique crystal structure and their uniform pores and channels allowed creating a large surface area and induced synergistic adsorption effects on bacteria. Zeolites have many applications in different fields such as petrochemical detergents, in construction and in the medical industry (Lemire et al., 2013a, 2013b; Li et al., 2018), however the ability of zeolites and modified zeolites to reduce bacteria (i.e. *E. coli* and *E. aerogenes*) is poorly documented. The obtained results (Fig. 7) indicated that zeolite has a low antibacterial activity against *E. coli* (3.5 mm of inhibition

zone) and none against *E. aerogenes*. TiO₂ nanoparticles are one of the antimicrobial agents used in water disinfection processes (Hossain et al., 2014). An increase in the use of TiO₂ nanoparticles in the industrial and consumer markets is concerning as there are still many questions regarding the risk assessment and exposure rates on humans and their impact on the environment (Ray et al., 2009). So, the development of novel materials with the standardization of minimum inhibitory concentrations is necessary. Hence, a way of reducing the dosage of TiO₂ nanoparticles is their combination with safe and environmentally friendly materials such as SiO₂ and zeolite. According to



A



B

Fig. 5. X-ray diffraction patterns parent zeolite (A) and, the synthesized Z-TiO₂ composites.

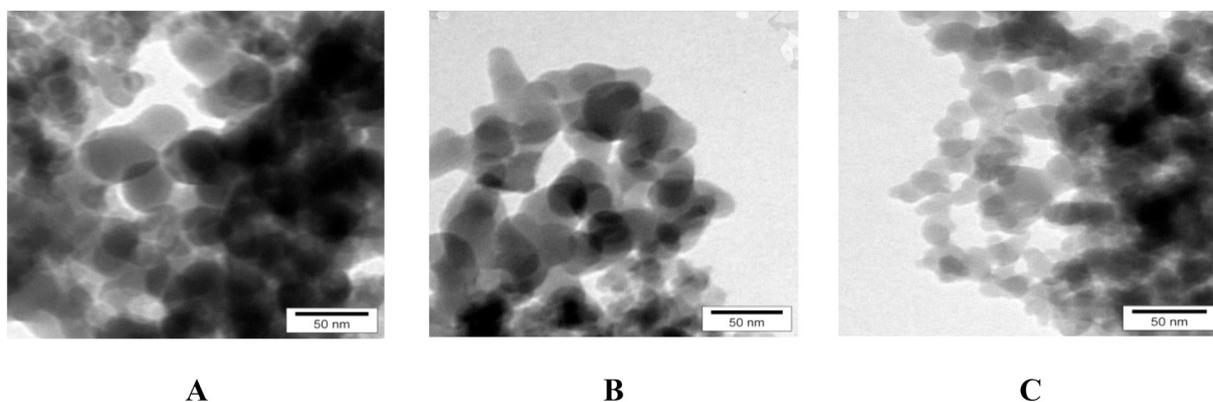


Fig. 6. Transmission Electron Microscopy (TEM) image of the synthesized $\text{SiO}_2\text{-TiO}_2$ nano particle composites.
Notes: Scale bars are 50 nm. (A) $5000\times$ magnification; (B) $10,000\times$ magnification; (C) $15,000\times$ magnification.

the obtained results, the SiO_2 nanoparticles showed the largest inhibition zones (i.e. 10.7 mm). Some studies reported that the number of the OH – groups on the surface of SiO_2 nanoparticles and their hydrophilic character increased the antibacterial activity of SiO_2 (Al-Jumaili et al., 2017; Sun et al., 2017). Several studies showed that TiO_2 itself has not antimicrobial activity against Gram negative bacteria such as *E. coli*, but its antimicrobial activity was enhanced in the presence of sunlight and other nano materials (Kalankesh et al., 2018). As it was observed in the present study, the Z- TiO_2 inhibition zone was rather higher than that of the parent zeolite (Hetrick et al., 2008). It was established that the modified zeolite with TTIP significantly improved the antimicrobial effect against *E. coli* (Tartanson et al., 2015). It is established that through their action mechanism in the bacteria, the chemical

substances, like antibiotics, can affect the bacteria cell wall while mammalian cells are preserved Z- TiO_2 is known as noncarcinogenic and nontoxic so it can be used as a disinfectant against *E. coli* in water treatment processes (Dal Lago et al., 2011; de Oliveira et al., 2012).

4. Conclusion

There is an increasing interest in developing novel antibacterial nanoparticles. Silica-based nanostructured materials appear to be particularly suitable alternatives to disinfection in water treatment process. Thus, in the present study $\text{TiO}_2\text{-SiO}_2$ hybrid nanoparticles and Z- TiO_2 composites were synthesized and their antibacterial activity investigated. All the synthesized materials showed antibacterial activity

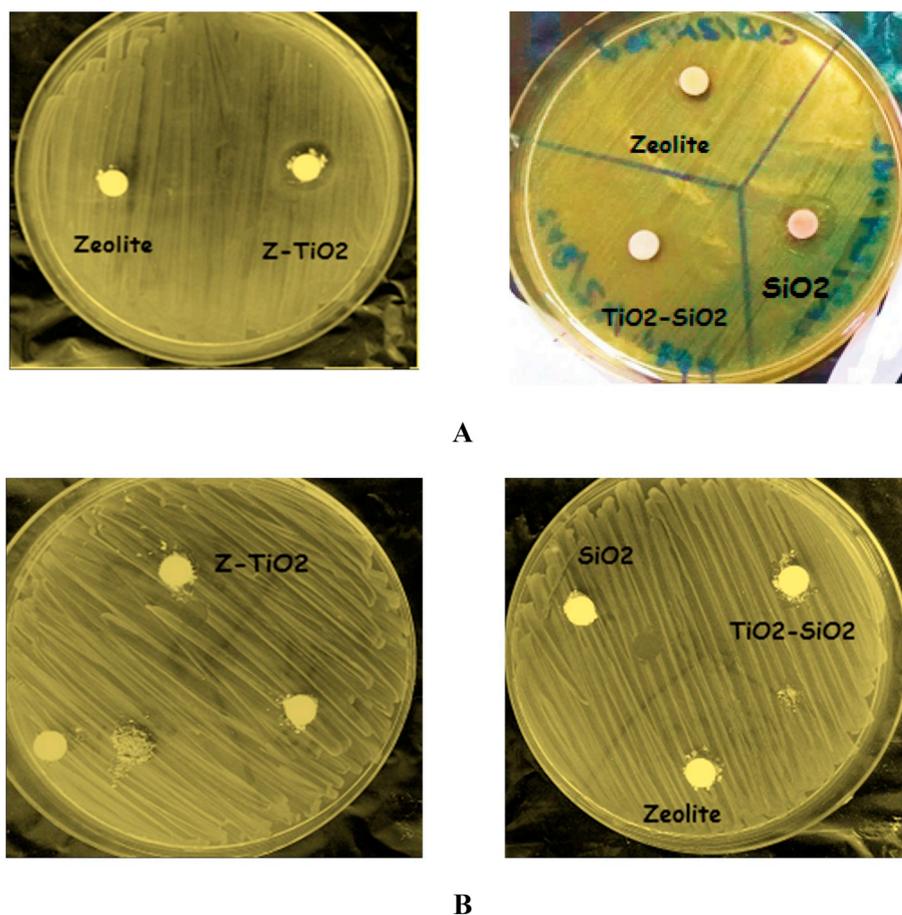


Fig. 7. Inhibition zone formed in the presence of Z- TiO_2 , $\text{SiO}_2\text{-TiO}_2$, zeolite and SiO_2 against *Echerichia coli* (A) and *Enterobacter aerogenes* (B).

against *E. coli* but not against *E. aerogenes*. The obtained results pointed out that the use of natural nanoparticles, such as SiO₂ and zeolite, which are regarded as noncarcinogenic and nontoxic, can be used as disinfectants against *E. coli* in water, providing, thus, a suitable alternative to the nonecological chlorine treatment.

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