**Preparation and investigation of hydrophilic, photocatalytic, and antibacterial
polyacrylic latex coating containing nanostructured TiO₂/Ag⁺-exchanged-
montmorillonite composite material**

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Abstract

In order to prepare a self cleaning and antibacterial coating, nanostructured TiO_2/Ag^+ -exchanged-montmorillonite composite material was prepared and used as additive in a commercial grade polyacrylic latex coating. FT-IR and UV–visible spectroscopy, X-ray diffraction patterns and FESEM were used to characterize the composition and structure of the nanocomposites and coatings. The polyacrylic coatings, prepared by the using of TiO_2/Ag^+ -exchanged-montmorillonite additive, showed better UV and visible light absorption, hydrophilic property, photodegradation of organic pollutants, stability in water and antibacterial properties than pristine commercial grade polyacrylic latex coating. According to the results, the modified polyacrylic coating containing 3%w of nanostructured TiO_2/Ag^+ -exchanged-montmorillonite composite material as additive, with TiO_2 to Ag^+ -exchanged-montmorillonite ratio of 2:1, was the best coating considering most of the useful properties such as low water contact angle, high photodegradation efficiency, and high water resistivity. The water contact angle for unmodified polyacrylic latex coating was 68° while it was decreased to about 10° or less for modified coating after 24h LED lamp illumination.

Keywords: Titanium dioxide nanoparticle; montmorillonite; hydrophilic; antibacterial; photocatalyst; polyacrylic coating

1. Introduction

Self cleaning coatings are coatings which can clean their own surface by themselves. This effect can be achieved through photocatalytic reactions and wettability of the surface (Midtdal and Jelle, 2013). Various semiconducting photocatalysts show self

cleaning property (Çakır et al., 2012; Kubacka et al., 2013). Among them, titanium dioxide (TiO₂) thin film coatings show the best photocatalytic and hydrophilic properties (Midtdal and Jelle, 2013).

TiO₂ as an important semiconductor has a band gap of 3.2 eV (Li et al., 2012). Titanium dioxide attracted much attentions and show potential applications in various fields such as air refining, wastewater treatment, self-cleaning coatings, and water self sterilization due to its high chemical stability, high photocatalytic activity, relatively low cost, and nontoxicity, high hydrophilicity and photocatalytic property which make the TiO₂ as a powerful oxidative material for pollution abatement through the generation of electrons and holes under light exposure (Olad and Nosrati, 2012a; Singh et al., 2013). When it rains and water hits to a hydrophilic self cleaning surface, thin sheets of water are formed on top of the surface which can wash off the photocatalytically broken down organic materials or inorganics and dusts in one movement (Midtdal and Jelle, 2013). TiO₂ nanoparticles show better photocatalytic and hydrophilic activities due to their large specific surface area (SSA) and therefore they exhibit higher self cleaning qualities (Jiang et al., 2011).

Due to the large band gap of TiO₂ nanoparticles, the activation process and production of electrons and holes are occur under UV irradiation (Midtdal and Jelle, 2013). Silver compounds are used as chemical sensitizers for red shifting of TiO₂ nanoparticles. They also show good antibacterial properties and are used for bacterial infection control in different areas (Huh and Kwon, 2011). The compositing of TiO₂ nanoparticles with Ag⁺ cations could enhance the antibacterial as well as photocatalytic and hydrophilic properties of the modified surfaces.

A major limitation of TiO₂ nanoparticles is their poor surface adsorption leading to the decreasing of photodegradation efficiency. Use of the solid adsorbents, for example

73 silica, alumina, zeolites, clays, and active carbon as the support for implantation of TiO₂
74 nanoparticles, can improve the availability of pollutant molecules on the surface of TiO₂
75 nanoparticles and increases the efficiency of photodegradation process (Ševčík et al.,
76 2009).

77 Clay minerals are layered aluminosilicates consisted of two different sheets. One sheet
78 containing tetrahedral SiO₄ units, in which each Si atom shares one O atom with the
79 second sheet containing aluminum in an octahedral lattice, represented as AlO₆ (Lopes
80 et al., 2014). It was well established that the improvement of the properties of clay
81 minerals containing composite materials, strongly depends on the level of clay mineral
82 dispersion in the matrix (intercalation or exfoliation). The insertion of different
83 materials into the interlayer spaces in the clay mineral causes to the increasing of d-
84 value. The exfoliated structure is made when the individual clay mineral layers are well
85 dispersed so that there is no interactions between them (Olad et al., 2012c). Silver ions
86 could exchange by interlayer cations in clay mineral structure which causes to the
87 increasing of d-value in clay mineral (Magaña et al., 2008). Montmorillonite (Mt)
88 because of its high cation exchange ability, swelling capacity, and a high SSA is among
89 the most commonly used layered clay minerals (Beltrán et al., 2013).

90 It seems that the preparation of nanostructured TiO₂/Ag⁺-exchanged-Mt composite
91 material as a hydrophilic and antibacterial material can be useful for the fabrication of
92 self cleaning coatings with enhanced photocatalytic and antibacterial properties.

93 In this idea, the modified TiO₂ nanoparticles are dispersed in the polymer binder of
94 coating and so modified coating is applied as self cleaning coatings. Also the
95 interactions between polymer matrix and dispersed modified TiO₂ nanoparticles can be
96 of worth for investigation. Acrylic polymers due to their good flexibility, good adhesion
97 strength, drying at room temperature, preparation of glossy coatings and high chemical

resistance as well as suitable price, gained much interest in coating industry. They are also important for outdoor applications because of their good resistance under outdoor conditions specially against degradation under the UV irradiation (Lombardi and Gasper, 2006). Self cleaning coatings based on acrylic polymers can be produced by the application of TiO_2 nanoparticles and modified TiO_2 nanoparticles. Also the hydrophilicity of polyacrylic coatings can be improved by using various surfactants to adjust surface tension and surface energy. Also the using of surfactants and polyvinylpyrrolidone can help to the better dispersion of TiO_2 nanoparticles and their nanocomposites as inorganic agents in organic polyacrylic based coatings (Fujishima et al., 2000; Basri et al., 2010; Carneiro et al., 2012)

The aim of this work is the preparation and characterization of nanostructured TiO_2/Ag^+ -exchanged-montmorillonite composite material and its application as additive in a commercial grade polyacrylic latex for the preparation of a transparent self cleaning industrial coating. Colorless coatings could use on glasses and painted surfaces without affecting their color, seeming and transparency. So in order to have the advantages of colorless coatings, lower contents up to 3% w of the prepared mineral additive were used in the formulation of coatings.

2. Experimental

2.1. Reagents and materials

TiO_2 nanoparticles (Degussa P25), montmorillonite KSF (SSA 20-40 m^2/g - Fluka chemicals), silver nitrate, and dodecyl benzene sulfonic acid (DBSA) surfactant (Merck Company), acrylic emulsion (Simab Resin Co. Iran, R-83), and polyvinylpyrrolidone (PVP, MW=360000, Sigma-Aldrich) were used in the preparation of modified polyacrylic coatings. Methylene blue (MB) dye was purchased from Merck Chemicals.

Mueller Hinton Broth (Scharlau Chemie S.A., European Union, Spain) and agar gepulvert (Merck Company) were used for antibacterial testing experiments.

2.2. Preparation of nanostructured TiO_2/Ag^+ -exchanged-Mt composite material

TiO_2 nanoparticles and Mt in different w/w ratios were dispersed in 25 mL aqueous AgNO_3 solution (0.01 M) by 1 minute sonication at 30 W power and were mixed for 30 h on a magnetic stirrer in darkness to ensure the uniformity of the dispersion and exfoliation of Mt layers and exchange of the cations of Mt by the silver ions. The so obtained powder product was filtered and washed with distilled water and dried.

2.3. Modification of polyacrylic latex by the nanostructured TiO_2/Ag^+ -exchanged-Mt composite material

A solution of 0.02 g PVP in 10 mL of distilled water was prepared. Different amounts of prepared nanostructured TiO_2/Ag^+ -exchanged-Mt composite material were dispersed in 2 mL of PVP solution in water followed by 20 sec sonication at 30 W power. 2 mL of polyacrylic latex was diluted with 4 mL of distilled water. 13.3 μL DBSA was added drop wise to 2 mL of diluted polyacrylic emulsion. Nanostructured TiO_2/Ag^+ -exchanged-Mt composite material, dispersed in PVP solution, was mixed with polyacrylic solution. 0.1 mL of prepared emulsion was casted on a 2 cm $\times$ 2 cm glass substrate and the coating was formed by the solvent evaporation. Prepared coatings were abbreviated as "a%T/AMb:c" in which "a" shows the percent of nanostructured TiO_2/Ag^+ -exchanged-Mt composite material in the polyacrylic emulsion, "T/AM" shows the nanostructured TiO_2/Ag^+ -exchanged-Mt composite material, and "b" and "c" exhibit the ratio (w/w) of TiO_2 nanoparticles to Mt in the nanocomposite.

2.4. Characterizations

2.4.1. FT-IR analysis

The FT-IR spectra of TiO₂ nanoparticles and nanostructured TiO₂/Ag⁺-exchanged-Mt composite materials were obtained using a FT-IR spectrometer (Bruker, Tensor 27 spectrophotometer, Germany). The samples were grounded and mixed thoroughly with potassium bromide. The FT-IR spectra of the pellets were then analyzed at the range of 400–4000 cm⁻¹ wavenumbers.

2.4.2. XRD analysis

The X-ray diffraction (XRD) patterns of all samples were obtained using a Siemens D500 diffractometer with Cu K α radiation (λ =1.5418 Å) at room temperature, operating at a voltage of 35 kV. The experiments were done at a scan rate of 1 °/min⁻¹ for a scan range of 2 theta= 1° to 70°.

2.4.3. Study of morphology

The morphologies of samples were studied using a MIRA3 field emission scanning electron microscope (FESEM). Samples were coated with a thin layer of Au–Pd using a sputter coater. Size distribution of particles was determined using Manual Microstructure Distance Measurement software (Nahamin Pardazan Asia Co., Iran). Particle diameter size data were collected from FESEM images. The number of counts was 50 and one image analyzed to obtain each histogram. The standard deviation of the measurements for TiO₂ nanoparticles, and TiO₂ nanoparticles in T/AM1:1 sample were 7.0, and 5.9 respectively.

2.4.4. UV-vis spectroscopy

The UV-visible absorbance of MB containing aqueous solutions, prepared T/AM nanocomposites and coated coupons were recorded using a T80+ UV/VIS Spectrometer (PG Instruments Ltd).

2.5. Investigation of hydrophilicity

To evaluate the hydrophilicity of the coatings, the contact angle of a water droplet on the surface of coatings was measured. Contact angles were measured in air by sessile-drop method. A micro-injector was used for injection of a 1 μ l droplet of distilled water on the surface of coatings. Contact angle analysis of coatings was evaluated after various irradiation times under LED lamp light (LED lamp 7 w UniLight A-11N, China- with the light emitting wavelength range of 420 nm-780 nm). For each measurement the mean of 3 times measurement was reported. Imagej 1.47v software produced by Wayne Rasband, national institutes of health, USA was used to process the contact angle measurements.

2.6. Testing of photocatalytic property

The photocatalytic degradation of methylene blue dye molecules in aqueous solution by using of different modified polyacrylic coatings was investigated under LED lamp irradiation with light emitting wavelength range of 420 nm-780 nm. Modified and unmodified polyacrylic coatings were individually soaked in 7 milliliters of MB solution (1.5 mg.L⁻¹). Dye solutions containing coatings were held under LED lamp irradiation for definite times in order to perform the photocatalytic degradation reactions. During irradiation, the container was shaken to keep the solution homogeneous. The MB concentration was analyzed using a UV-Vis spectrophotometer

at the wavelength of 664 nm. The UV–Vis absorption spectrum and calibration graph of MB dye solution were shown in supplementary information as Fig. S1 and S2 respectively. Equation and R-squared value obtained from calibration curve were $y=0.1731x-0.0275$ and 0.972 respectively. The photodegradation efficiency (R%) was calculated using Eq. 1:

$$R\%=100[(C_0-C)/C_0] \quad \text{Eq. 1}$$

where C_0 is the initial concentration of MB dye in solution, C is the concentration of MB at each time duration in photodegradation process, and R is the photodegradation efficiency.

2.7. Water resistance testing

Water resistance testing was performed by soaking the coatings in distilled water and evaluation of the degree of peeling off from the underlying glass substrate visually. Peeling off the coatings was exhibited by numbers. The numbers show 5:nil, 4:few, 3:medium, 2:much and 1:peeled.

2.8. Antibacterial testing

The coatings were individually tested against two Gram negative and three Gram positive bacteria including *S. aureus* ATCC 6538, *L. monocytogenes* ATCC 19118, *S. typhimurium* ATCC 13311, *E. coli* ATCC 43894, and *B. anthracis*. The last bacteria had been obtained and identified from clinical specimens in microbiology laboratory in veterinary faculty, University of Tabriz, Tabriz, Iran and was subsequently maintained as stock strains by storage in freeze-dry form.

The sterile glass substrates (1 cm ×1 cm) were coated with 50 µl of polyacrylic latex modified with 1%T/AM1:1 additive. Fresh cultures of bacteria was inoculated on

nutrient broth and incubated for 24 hour at 37°C. Adequate amount of Muller- Hinton agar was poured into the sterile plate until to be solid. The glasses were impregnated in the inoculated agar. Negative controls were prepared using unmodified polyacrylic latex. The inoculated plates were incubated at 37°C under LED lamp light illumination (with the light emitting wavelength range of 420 nm-780 nm) for 24 h. Antibacterial activity was evaluated by measuring the inhibition zones in reference to the test organisms.

3. Results and discussion

3.1. FTIR studies

The pristine TiO₂ nanoparticles and nanostructured TiO₂/Ag⁺-exchanged-Mt composite material were characterized using FTIR technique (Fig. 1). As shown in the FTIR spectrum of pristine TiO₂ nanoparticles (Fig. 1a), the characteristic peak of TiO₂ nanoparticles (Ti-O stretching mode) was appeared at 450 cm⁻¹ (Jamal et al., 2014). In the FTIR spectrum of nanostructured TiO₂/Ag⁺-exchanged-Mt composite material with TiO₂ to Ag⁺-exchanged-Mt ratio of 1:1 (Fig. 1b), the characteristic peaks at 467 cm⁻¹ and 1047 cm⁻¹ are attributed to Ti-O bond and asymmetric stretching vibrations of bridge bonds of Si-O (Si) and Si-O (Al) respectively (Peter et al., 2012). The peak related to the stretching mode of Ti-O in nanostructured TiO₂/Ag⁺-exchanged-Mt composite material was shifted to higher wavenumbers versus to the pristine TiO₂ nanoparticles. This indicates the presence of some interactions between TiO₂ nanoparticles, Mt, and Ag⁺ cations. In other words, it demonstrates the presence of physicochemical interactions between TiO₂ nanoparticles and Ag⁺-exchanged-Mt.

3.2. X-ray diffraction analysis

The analysis of X-ray diffraction (XRD) patterns was employed to investigate the structure of nanostructured TiO₂/Ag⁺-exchanged-Mt composite material. The XRD patterns of Mt, TiO₂ nanoparticles and nanostructured TiO₂/Ag⁺-exchanged-Mt composite material with TiO₂ to Ag⁺-exchanged-Mt ratio of 1:1, were shown in Fig. 2. The characteristic reflections of Mt and TiO₂ nanoparticles are recognizable in Fig 2a and b respectively (Olad et al., 2012b; Olad et al., 2014). The XRD patterns of nanostructured TiO₂/Ag⁺-exchanged-Mt composite material (Fig. 2c), showed the characteristic reflections of both TiO₂ nanoparticles and Mt mineral which reveals that both components are present in the T/AM1:1 nanocomposite. Reflections for orthorhombic structure of AgNO₃ (JCPDS, File No. 43-0649) which indicate the presence of the unreacted AgNO₃ as impurity were not seen in Fig. 2c. Considering the main reflection in the X-ray diffraction patterns of the Mt ((001) reflection) in Fig.2c, the formation of interlayer spaces in Mt by regular stacking of the silicate layers can be concluded. According to the results, the characteristic reflection peak for pristine Na⁺-Mt (Fig. 2a) was appeared at 2θ=7.49° with the corresponding d-value of 11.79Å° calculated using Eq. 2 (Bragg equation):

$$n\lambda = 2d\sin\theta \quad \text{Eq. 2}$$

where n is an integer determined by the order given, λ is the wavelength of X-ray radiation, d is the interlayer space between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes. A broad amorphous reflection of Mt (001) was seen in the XRD patterns of nanostructured TiO₂/Ag⁺-exchanged-Mt composite material (Figure 2c) which indicates the exfoliated-intercalated structure of Mt in the prepared T/AM1:1 nanocomposite. Entering of Ag⁺ cations or TiO₂ units between the layers of Mt could increase the d-value or shed in layers of Mt planes.

Shifting of the basal reflection (001) from $2\theta=7.49^\circ$ for the original montmorillonite sample to $2\theta=6.27^\circ$ for the nanostructured TiO_2/Ag^+ -exchanged-Mt composite material sample and decreasing the intensity of basal reflection approve the exfoliated-intercalated structure of layers of Mt planes in T/AM1:1 sample (Sun et al., 2015). Upon the intercalation of Ag^+ cations or TiO_2 units into the montmorillonite structure, four new reflections ($2\theta=8.85^\circ$, 12.51° , 17.87° , and 45.67°) were emerged (Fig. 2c). Interactions between the components of the T/AM nanocomposite can promote the formation of some structures. Moreover, these structures could be formed in the preparation of the composite materials. Since it was difficult for TiO_2 units to be intercalated into the interlayer spaces of Mt and some of them were immobilized on the Mt layer surfaces, it can be causes to the packing of some of the Mt layers and making a new reflection peak at $2\theta=8.85^\circ$ (Yuan et al., 2011). Due to the presence of various atoms in Mt structure and their various tendency to interact with TiO_2 units or Ag^+ cations and prepare new structures, new reflections can be made and appeared. In other word the new reflection peaks may refer to the special new structures in the prepared T/AM nanocomposite which their exactly recognition is difficult.

3.3. UV-Vis spectroscopic analysis

The UV-Vis spectra of Mt, pristine TiO_2 nanoparticles and nanostructured TiO_2/Ag^+ -exchanged-Mt composite material with different TiO_2 to Ag^+ -exchanged-Mt ratios were recorded and analyzed to investigate the effect of compositing of the TiO_2 and Ag^+ -exchanged-Mt, on the light absorption characteristics of TiO_2 nanoparticles. The UV-Vis spectra of nanostructured TiO_2/Ag^+ -exchanged-Mt composite materials and their components were shown in Fig. 3. TiO_2 nanoparticles strongly absorb UV light but slightly absorb visible light irradiation (Fig. 3a) which indicates that UV range of light

spectrum could cause to the excitation of electrons that present in the valence band, to the conducting band of TiO₂ nanoparticles. The UV-Vis absorption of Mt is very weak with respect to the other specimens, so the absorption peak related to the Mt (Fig. 3e) was appeared near the base line in Fig. 3. The UV-Vis spectra of nanostructured TiO₂/Ag⁺-exchanged-Mt composite materials with TiO₂ to Ag⁺-exchanged-Mt ratios of 2:1, 1:1 and 1:2 were shown in Figs. 3b, c and d respectively. Increasing of the TiO₂ to Ag⁺-exchanged-Mt ratio causes to the increasing of the light absorption of T/AM nanocomposite in UV and visible light regions. The presence of TiO₂ nanoparticles increases the absorbance of electromagnetic spectrum by T/AM nanocomposites. The UV-Vis spectra of unmodified polyacrylic latex coating and polyacrylic latex coating modified by using of T/AM1:1 were investigated (Fig. 4). The UV-Vis spectrum of polyacrylic latex coating without any additive was shown in Fig. 4a. The UV-Vis spectra of polyacrylic latex coatings modified by 0.25%, 0.5%, 1%, 2% and 3% of T/AM1:1nanocomposite additive were represented in Figs. 4b, c, d, e and f respectively. By increasing of the additive percent in polyacrylic latex, absorption of light by the coating is increased.

3.4. Band gap calculation

To estimate the band gap of Mt, pristine TiO₂ nanoparticles and nanostructured TiO₂/Ag⁺-exchanged-Mt composite materials with different TiO₂ to Ag⁺-exchanged-Mt ratios, the related UV-Vis spectra can be useful. The optical band gap of the samples was determined by the application of the Tauc model (Tauc, 1974) as well as the Davis and Mott model (Davis and Mott, 1970). In the high absorbance region the band gap was obtained using the equation 3.

$$ah\nu = D(h\nu - E_g)^n \quad \text{Eq. 3}$$

where $h\nu$ is the photon energy, a is the absorbance, E_g is the optical band gap, and D is a constant. For a direct transition, $n=1/2$ or $2/3$ is suitable, and the former value is found to be more appropriate for TiO_2 nanoparticles since it gives the best linear curve in the band-edge region. The E_g value can be obtained by extrapolating of the linear portion of the $(ah\nu)^2$ to $h\nu$ curve. The obtained optical band-gap values are summarized in Table 1. The calculated band gap is found to be about 3.25 eV for TiO_2 nanoparticles, which is greater than the reported band gap value for TiO_2 nanoparticles, $E_g = 3.2$ eV (Li et al., 2012). The difference in the band gap values ranging from 3.25 and 3.2 eV is one of the curious features of the literature on TiO_2 nanoparticles. Optical band gap differs from electrical band gap because of Bursteine-Moss effect. Equation 4 shows this effect.

$$E_O = E_g + \Delta E_{BM} \quad \text{Eq. 4}$$

where E_O is optical band gap, E_g is electrical band gap, and ΔE_{BM} is Bursteine-Moss shift. Absorption is measured at room temperature. At this temperature, the band gap of a semiconductor is increased since the absorption edge is shifted to higher energy values as a result of the population of all states close to the conduction band (Bidadi et al., 2013).

As summarized in Table 1, the band gap of Mt is 5.12 eV. The Mt mineral because of its large band gap, can be excited very little by the electromagnetic irradiation (Fig. 3). Nanostructured TiO_2/Ag^+ -exchanged-Mt composite materials show different band gaps with respect to TiO_2 nanoparticles. The band gaps of T/AM2:1, 1:1, and 1:2 nanocomposites are 2.99, 2.9 and 3.1 eV respectively. Compositing of large band gap Mt with TiO_2 nanoparticles could increase the band gap of TiO_2 nanoparticles, but the presence of conductive silver ions in the structure of Mt causes to the reduction of TiO_2 band gap. Contest between these two phenomena causes to the decreasing or increasing of band gap of composites with respect to neat TiO_2 nanoparticles. Creation of the new

bands in the space between the valence band and conduction band of TiO₂ nanoparticles in T/AM2:1, T/AM1:1, and T/AM1:2 nanocomposites, causes to the reduction of the band gap of TiO₂ nanoparticles. The T/AM1:1 nanocomposite showed lowest band gap.

3.5. Morphological studies

Field emission scanning electron microscopy (FESEM) was used to investigate the surface morphology of Mt, TiO₂ nanoparticles, T/AM1:1 and polyacrylic latex coating modified by 1%T/AM1:1 (Fig. 5). Mt aluminosilicate showed layered structure in nano scale level (Fig. 5a) with d-value of about 1.18 nm obtained by using XRD pattern data (Fig. 2a) analysis. A higher magnification FESEM image of Mt aluminosilicate with magnification of $\times 100,000$ was provided and shown in Fig. 5a. The FESEM images of TiO₂ nanoparticles and their size distribution were shown as Fig. 5b and e respectively. The average diameter of TiO₂ nanoparticles is about 30-40 nm. FESEM image of T/AM1:1 (Fig. 5c) confirmed the presence of TiO₂ nanoparticles on the surface of Mt compared to the pristine Mt (Fig 5a). Size distribution of TiO₂ nanoparticles on the Ag⁺-exchanged-Mt is shown in Fig. 5f which indicates that most of TiO₂ nanoparticles are in the size range of 30 to 40 nm, but the peak of size distribution curve was shifted to bigger size values than that of pristine TiO₂ nanoparticles. This result indicates that compositing of TiO₂ nanoparticles by Mt causes to a little aggregation of immobilized TiO₂ nanoparticles on Mt layers. FESEM micrograph of polyacrylic latex coating modified by 1%T/AM1:1 was shown in Fig. 5d that indicates the formation of a uniform surface with additive particles. Decreased size of immobilized TiO₂ nanoparticles with respect to pristine TiO₂ nanoparticles (Fig. 5b) and immobilized TiO₂ nanoparticles on the Ag⁺-exchanged-Mt (Fig. 5c) indicate the good dispersion of additive in polymer matrix.

3.6. Contact angle measurement

The sessile drop method was employed for the measurement of contact angle between the coatings surface and distilled water. The water contact angle values on different coating samples before and after exposure to LED lamp light irradiation were exhibited in Table 2. The contact angle between water and unmodified polyacrylic latex was 65°, so the commercial grade polyacrylic latex is partially wetted by water. By irradiation of light, the contact angle was increased slowly which means that the light irradiation may causes to the slowly degradation of the polymer molecules and causes to the variation of contact angles before and after light irradiation. By the addition of additives to commercial grade polyacrylic latex, considerable decrease in the contact angles was seen (Table 2). Also the reduction in contact angles before and after light exposure can be seen for formulated coatings. The reason for the reduction of contact angle for formulated polyacrylic coatings (before light irradiation) is the presence of surfactant in the coatings formulation. Surfactants because of their ability in adjusting surface tension and surface energy could make the surface hydrophilic (Fujishima et al., 2000; Carneiro et al., 2012). Equal amounts of a surfactant in different coatings caused to similar changes (reduction) in contact angle for T/AM nanocomposite contained coatings before light irradiation and so caused to similar hydrophilic properties in coatings. TiO₂ nanoparticles in the presence of light irradiation could show good hydrophilicity (Fujishima et al., 2000). It can be seen from Table 2 that the water contact angle decreases with increasing light illumination time for all modified polymer coatings. TiO₂ is a semiconductor with a band gap of about 3.2 eV and electromagnetic irradiation can excite the TiO₂ electrons from valence band to conduction band and leave holes in the valence band. The produced electrons tend to reduce the Ti(IV)

cations to the Ti(III) state, and the holes oxidize the O^{2-} anions. Therefore oxygen atoms are ejected and create oxygen vacancies that water molecules can then occupy these vacancies and produce adsorbed OH groups. OH groups tend to make the surface hydrophilic (Fujishima et al., 2000). Compositing of TiO_2 nanoparticles with Ag^+ -exchanged-Mt decreased the band gap of TiO_2 nanoparticles (Table 1). So the nanostructured TiO_2/Ag^+ -exchanged-Mt composite materials could be excited by lower energy electromagnetic irradiation than that of pristine TiO_2 nanoparticles and show better hydrophilic properties under natural light irradiation. With increasing the percent of additives in coatings, water contact angles are decreased slightly. Commercial grade polyacrylic coatings containing 3%T/AM2:1 showed the best hydrophilic behavior under 24 h LED lamp light irradiation. For comparison, water contact angles of polyacrylic coating modified by 1% pristine TiO_2 nanoparticles were reported in Table 2. Before light illumination, contact angle of coating was 11° that is very smaller than that of T/AM nanocomposite contained coatings. Additive used in this coating is pristine TiO_2 nanoparticles and presence of larger amounts of TiO_2 nanoparticles in additive could show hydrophilicity effect even in the little light irradiation presence in the dark environment. By LED lamp light irradiation, water contact angle of TiO_2 contained coatings was decreased very slightly and after 24 hour light exposure, the contact angle was 9° .

Quagliarini and coworkers coated TiO_2 on stone surfaces and observed 20 degrees contact angle after 50 min UV light irradiation (Quagliarini et al., 2013). In this work a few amount of composite additive (maximum 3%) was used in coating formulation and contact angles, measured under LED lamp light irradiation (with the light emitting wavelength range of 420 nm-780 nm), were less than 20 degrees after 4 h light irradiation. Comparison of two conditions shows effectiveness of our research.

3.7. Photocatalytic property

The photocatalytic activity of unmodified commercial polyacrylic coating and the polyacrylic coating modified with nanostructured TiO_2/Ag^+ -exchanged-Mt composite material in degradation of MB dye molecules under LED lamp irradiation was evaluated and compared (Figure 6). Some dye molecules may decompose under natural light irradiation. Therefore, it is important to know the extent to which the MB dye molecules are photolyzed if no catalyst was used and hence to estimate the contribution of direct photolysis in the overall decomposition process. For this, the decomposition of MB under LED lamp light irradiation was examined in the absence of any coating (Fig. 6a, no photocatalyst). It was found that MB dye molecules are photolyzed less than 3% under LED lamp light irradiation for 300 min; so the contribution of direct photolysis in the overall decomposition process is negligible. Degradation of MB under LED lamp light irradiation in the presence of pristine polyacrylic coating was investigated (Fig. 6a, unmodified polyacrylic coating). Unmodified polyacrylic coating could degrade less than 3% of MB dye molecules under 300 min LED lamp light irradiation, that big fraction of this degradation is relevant to direct photolysis. Degradation of MB molecules at less than 5 hours of irradiation by LED lamp light in the presence of 1% TiO_2 nanoparticles contained polyacrylic coating was reached to 28%. The photodegradation efficiency (R%) of MB during photocatalytic decomposition using different T/AM2:1 contained polyacrylic latex coatings was shown as Fig. 6b. In all coatings containing various percents of T/AM2:1 additive, photodegradation efficiency is increased by increasing of the exposure time. By increasing the percent of T/AM2:1 additive from 0.25% to 3%, photodegradation efficiency increases in a definite degradation time. However the coating containing 2%T/AM2:1 additive showed a little

higher photodegradation efficiency than that of coating containing 3%T/AM2:1 additive. The coating containing 2%T/AM2:1 additive showed 70% photodegradation efficiency after 300 min light irradiation. The photodegradation efficiencies (R%) of MB during photocatalytic decomposition using different T/AM1:1 and T/AM1:2 contained polyacrylic latex coatings were shown in Fig. 6c and d respectively. In all coatings containing different percents of T/AM1:1 and T/AM1:2 additives, photodegradation efficiency increases by increasing the light exposure time. Generally, increasing the percent of T/AM1:1 and T/AM1:2 additives from 0.25% to 3%, increases photodegradation efficiency in a definite degradation time. The coatings containing 3%T/AM1:1 and 3%T/AM1:2 additives show the highest photodegradation efficiencies in the T/AM1:1 and T/AM1:2 contained coatings after 300 min light irradiation respectively. The photodegradation efficiency of 3%T/AM1:1 and 3%T/AM1:2 contained coatings after 300 min LED lamp light irradiation were 47% and 66% respectively. Photodegradation efficiencies achieved by using coatings containing 1%T/AM nanocomposites are higher than that of coatings containing 1% pristine TiO₂ nanoparticles that approve the high efficiency of prepared T/AM nanocomposites in producing coatings with improved photocatalytic property. Nanostructured TiO₂/Ag⁺-exchanged-Mt composite material is excited under light irradiation which causes to the photogeneration of electron-hole pairs and achieving of photocatalytic activity. Generated holes can reach to the surface of photocatalyst where they can make contact with the MB dye molecules and cause to their degradation. Photogenerated electrons can also react with oxygen and produce superoxide anion radicals. These radicals may form hydrogen peroxide or organic peroxides in the presence of oxygen and organic molecules like MB. Hydrogen peroxide can form hydroxyl radicals which are powerful oxidizing agents. Produced radicals are capable of attack to the organic pollutants like

MB dye molecules and cause to their degradation (Olad and Nosrati, 2012a). Awazu and coworkers considered the rate of decomposition of MB molecules on the TiO₂ film immobilized on the Ag⁺/SiO₂ core-shell structure which was five times faster than that of TiO₂ alone (Awazu et al., 2008). In our work, results showed that the use of Ag⁺-exchanged-Mt as compositing with TiO₂ nanoparticles efficiently improves the photocatalytic property of TiO₂ nanoparticles and higher photodegradation efficiency were obtained with the use of coatings containing T/AM nanocomposites than that of coating containing pristine TiO₂ nanoparticles.

3.8. Water resistance

The results of water resistance tests were shown in Fig. 7. The Y axis shows the adhesion quantity of coatings to underlying substrate in accordance to the peeling off of the coatings from the surface in the distilled water as 5: nil, 4: few, 3: medium, 2: much, and 1: peeled. Water resistance of the unmodified polyacrylic latex coating and the coating modified with 1% TiO₂ nanoparticles were shown in Fig 7a. Unmodified polyacrylic coating and coating modified with 1% TiO₂ nanoparticles are completely peeled off after 30 min and 75 min of soaking in distilled water respectively. Figs. 7b, c and d show water resistance of the coatings containing T/AM2:1, T/AM1:1 and T/AM1:2 additives respectively. It can be seen that the polyacrylic latex coatings modified by T/AM nanocomposite additives are more water resistant than unmodified polyacrylic latex coating or pristine TiO₂ contained coating. Generally, with increasing the percent of T/AM nanocomposite additives, water resistivity is increased and the peeling is postponed. The coating containing TiO₂ to Ag⁺-exchanged-Mt ratio of 2:1 with 2% and 3% additive showed the best water resistivity.

3.9. Antibacterial testing

L. monocytogenes, *B.anthraxis* and *S. aureus* as gram positive and *E. coli* and *S. thyphimurium* as Gram negative species were subjected to the unmodified and modified polyacrylic latex coating with 1%T/AM1:1 additive to determine the antibacterial effect of the coatings. Coatings were casted on the both of glass coupons and discs. As shown in Fig. 8, Gram positive species (Fig. 8a, b and c) were showed to have no growth zone around the modified polyacrylic coatings but not around unmodified polyacrylic latex coatings. As silver ions leached from the modified polyacrylic coating into the solution, they could migrate to the agar surface next to the discs (Bedi et al., 2012). This could prevent any growth of Gram positive bacteria species in the immediate vicinity of the coating. When the Gram negative species subjected to the unmodified and modified polyacrylic latex no growth zone was not seen. Therefore prepared modified polyacrylic latex with 1%T/AM1:1 additive couldn't prevent any growth of Gram negative bacteria species. The inhibitory effect of Ag ions under a complex physiological condition, is believed to be due to its sorption to the negatively charged bacterial cell wall (in both Gram positive and Gram negative bacteria), deactivating cellular enzymes, disrupting membrane permeability, and finally leading to bacteria lysis and death (Colon et al., 2006; Osamu et al., 2004; Zhu et al., 2004; Choi et al., 2008). By the way different results were shown by titanium dioxide nanoparticles in two Gram positive and two Gram negative bacteria (Bonnet et al., 2015). Antibacterial property of TiO₂/Ag/TiO₂ sandwich films appeared equally potent in eliminating the bacteria when applied to both the Gram positive (*S.aureus* and *Streptococcus pyogenes*) and Gram negative (*E.coli* and *Acinetobacter baumannii*) bacteria. These results were not constant with the results of other studies which showed better activity of the silver ion against the Gram negative *E.coli* than against the Gram positive *S.aureus* (Jung et al., 2008). It seems, bilayer lipid

of outer membrane of Gram negative bacteria with hydrophobic properties prevent the prepared hydrophilic T/AM nanocomposite additive to approach the bacteria and destruct them. Further studies are needed in order to elucidate mechanisms of toxicity induced by our T/AM nanocomposite, so it could be interesting to determine intracellular ROS concentration, lipid peroxidation level, membrane integrity and DNA damage.

4. Conclusions

A hydrophilic, photocatalytic, and antibacterial coating based on a commercial polyacrylic latex was prepared and investigated. Nanostructured TiO_2/Ag^+ -exchanged-montmorillonite composite material with various TiO_2 to Ag^+ -exchanged-montmorillonite ratios were used as self cleaning and antibacterial agent in formulation. Polyacrylic coatings containing nanostructured TiO_2/Ag^+ -exchanged-montmorillonite composite material additives, showed better UV and visible light absorption, hydrophilic properties, photodegradation of organic pollutants, stability in water and antibacterial properties than that of pristine commercial grade polyacrylic latex coating. Polyacrylic coating modified with 3%T/AM2:1 showed the lowest contact angle after 24 h LED lamp light irradiation.

The contact angle for unmodified polyacrylic latex coating was 68° which was decreased to less than 10° in the coating modified by 3%T/AM2:1 after 24h LED lamp illumination. Also this modified coating showed high photodegradation efficiency and high water resistivity. Therefore the polyacrylic based coating containing 3% of nanostructured TiO_2/Ag^+ -exchanged-montmorillonite composite material additive with TiO_2 to Ag^+ -exchanged-montmorillonite ratio of 2:1 is proposed as the best coating formulation.

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Figures and Tables Captions

Table 1 Optical band-gap values of nanostructured TiO₂/Ag⁺-exchanged-Mt composite material and its individual components

669

670 **Table 2** Water contact angle values of the commercial grade polyacrylic resin coatings
671 containing nanostructured TiO_2/Ag^+ -exchanged-Mt composite material before and after
672 exposure to LED lamp light

673

674 **Fig. 1** FTIR spectra of TiO_2 nanoparticles (a) and nanostructured TiO_2/Ag^+ -exchanged-Mt
675 composite material (b)

676

677 **Fig. 2** XRD patterns of montmorillonite (a), TiO_2 nanoparticles (b), and T/AM1:1
678 nanocomposite (c)

679

680 **Fig. 3** UV-Vis spectra of TiO_2 nanoparticles (a), nanostructured TiO_2/Ag^+ -exchanged-Mt
681 composite material with TiO_2 to Ag^+ -exchanged-Mt ratios of 2:1 (b), 1:1 (c) and 1:2 (d)
682 and montmorillonite (e)

683

684 **Fig. 4** UV-Vis spectra of unmodified (a) and modified commercial grade polyacrylic resin
685 coating with 0.25% (b), 0.5% (c), 1% (d), 2% (e) and 3% (f) of T/AM1:1
686 nanocomposite additive

687

688 **Fig. 5** FESEM micrographs of montmorillonite (a), TiO_2 nanoparticles (b), T/AM1:1
689 nanocomposite (c), modified commercial grade polyacrylic resin coating with
690 1%T/AM1:1 (d), diameter size distribution of TiO_2 nanoparticles (e), and TiO_2
691 nanoparticles in T/AM1:1 (f)

692

693 **Fig. 6** Photodegradation efficiency of MB dye by using unmodified (a), and modified
694 commercial grade polyacrylic resin coating with various amounts of T/AM2:1 (b),
695 T/AM1:1 (c), and T/AM1:2 (d) additives against time during LED light irradiation

697 **Fig. 7** Water resistance of unmodified (a) and modified commercial grade polyacrylic resin
698 coating with different percent of nanostructured TiO_2/Ag^+ -exchanged-Mt composite
699 materials additive with TiO_2 to Ag^+ -exchanged-Mt ratios of 2:1(b), 1:1(c) and 1:2(d).
700 The numbers in Y axis is 5:nil, 4:few, 3:medium, 2:much and 1:peeled

702 **Fig. 8** Results of the antibacterial activity of unmodified (non starred) and modified
703 commercial grade polyacrylic resin coating with 1%T/AM1:1 (starred) in *L.*
704 *monocytogenes* (a), *B. anthracis* (b), *S. aureus* (c), *E. coli* (d) and *S. thyphimurium* (e)
705 agar plates.

Table 1

Sample name	Band gap (eV)
TiO ₂ nanoparticles	3.25
Montmorillonite	5.12
Nanostructured TiO ₂ /Ag ⁺ -exchanged-montmorillonite composite material 2:1	2.99
Nanostructured TiO ₂ /Ag ⁺ -exchanged-montmorillonite composite material 1:1	2.90
Nanostructured TiO ₂ /Ag ⁺ -exchanged-montmorillonite composite material 1:2	3.10

Table 2

Coating		Contact angle (°) before light irradiation	Contact angle (°) after 4h light irradiation	Contact angle (°) after 24h light irradiation
Unmodified polyacrylic	unmodified	65	70	68
Modified polyacrylic with	1% pristine TiO ₂	11	10	9
	0.25% T/AM 1:2	37	23	16
	0.5% T/AM 1:2	33	17	14
	1% T/AM 1:2	38	19	13
	2% T/AM 1:2	29	15	11
	3% T/AM 1:2	27	13	11
	0.25% T/AM 1:1	33	15	11
	0.5% T/AM 1:1	36	14	11
	1% T/AM 1:1	35	13	10
	2% T/AM 1:1	38	17	11
	3% T/AM 1:1	33	17	10
	0.25% T/AM 2:1	35	30	12
	0.5% T/AM 2:1	35	21	11
	1% T/AM 2:1	35	21	10
	2% T/AM 2:1	38	14	12
	3% T/AM 2:1	39	17	6

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8