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Synthesis of nanocomposite based on Semnan natural zeolite for photocatalytic degradation of tetracycline under visible light

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ABSTRACT

This study investigated the photocatalytic behaviors for the nanocomposite of TiO₂ P25 and Semnan natural zeolite in the decomposition of tetracycline under visible light in an aqueous solution. The structural features of the composite were investigated by a series of complementary techniques that included X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), surface area (BET) measurement, and ultraviolet-visible diffuse reflectance spectroscopy (DRS). The surface area measurement disclosed an enhancement of surface area by ~2 times for the synthesized TiO₂/Semnan natural zeolite than that of commercial TiO₂ P25. The asprepared photocatalyst (TiO₂/Semnan natural zeolite) showed pH dependence and more than 87% of the tetracycline could be degraded from the solution under visible irradiation within 90 min at a pH of 6. This excellent catalytic ability was mainly attributed to the hybrid effect of the photocatalyst and adsorbent. The results provided new insight into the performance of active photocatalysts on the treatment of pharmaceutical wastewater. In addition, the immobilization of TiO₂ onto Semnan natural zeolite permitted easier separation of the adsorbent from the treated water.

1. Introduction

Pharmaceutical antibiotics are used extensively worldwide in human therapy and the farming industry [1, 2]. Among all the antibiotics, tetracycline (TC) is one of the most widely used in aquaculture and veterinary medicines. Exposure to antibiotic residues and their transformed products could cause a variety of adverse effects, including acute and chronic toxicity and antibiotic resistance [3]. This resistance can be transmitted to humans through complex biochemical transference processes [1]. Hence, the removal or degradation of pharmaceutical pollutants is an important research subject. Considerable efforts have been devoted to developing a suitable purification method that can easily destroy these bio-recalcitrant organic contaminants [4]. Due to their antibacterial nature, antibiotic residues cannot be effectively eliminated by traditional biological methods. Several studies have shown that the biodegradation of certain antibiotics is low during wastewater

treatment [4, 5]. Most conventional wastewater treatment plants, which employ processes such as activated carbon adsorption, membrane filtration, chemical coagulation, ion exchange on synthetic adsorbent resins, etc., are inefficient in the removal of TC antibiotics. Also, they generate wastes during the treatment of contaminated water which requires additional steps and cost [1]. Nowadays, it is well confirmed that advanced oxidation processes (AOPs) are the most recommended technologies for the removal of different pollutants from water [5]. Heterogeneous photocatalysis oxidation is the most popular AOP method and has been widely used for the removal of water pollutants because of its advantages, especially its capability to be employed under ambient conditions [4, 6-10]. In past decades, titanium dioxide semiconductor (TiO₂) has attracted great interest due to its photocatalytic properties. It is inexpensive, non-toxic, stable, and potentially reusable in water [4, 11]. Zhu et al. [12] used nano sized TiO₂ (P25) as a photocatalyst and studied its ability

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for TC degradation. More than 95% of the TC was removed within 40 min (40 ppm of TC, 1 g/L of TiO₂) under UV irradiation. Recent publications indicate that TC is completely oxidized by photocatalysis in short time periods [1, 4]. The TC degradation efficiency changes by different degrees with respect to different operating conditions. However, the practical applications of TiO₂ as an adsorbent or a photocatalyst in aqueous solutions are limited because of the recovery problems of fine TiO₂ particles [13]. Recently, attempts have been made to immobilize the TiO₂ particles on different supports, such as activated carbon [14], clay [15] and zeolites [16], to improve their separation from bulk water [17]. Zeolites are three dimensional alumino silicate minerals with a porous structure that have valuable physicochemical properties, such as cation exchange, molecular sieving, catalysis and adsorption [16, 17]. Natural zeolites are cheap, abundant and easily available [17]. It is a promising support for TiO₂ because they have regular pores and channels that can confine substrate molecules, thereby enhancing adsorption and photocatalysis. TiO₂ supported on zeolite combines the adsorptive capability of zeolite with the photocatalysis behavior of TiO₂, thus resulting in a synergistic and enhanced degradation efficiency. A zeolite/TiO₂ composite adsorbent that is easily recoverable via TiO₂ photocatalytic oxidation will lead to a cost-effective and environmentally friendly water treatment process, thus avoiding the production of waste or need for a high cost regeneration process. A simple method for combining TiO₂ with adsorbents involves the mechanical mixing of TiO₂ powders into adsorbents powders. Some researchers have utilized this method using zeolites as the adsorbent and applied the resulting photocatalyst for the purification of water [18]. In this work, the particles of an Iranian natural zeolite were used to obtain TiO₂/natural zeolite as a heterogeneous catalyst for the degradation of a TC pharmaceutical capsule in an aqueous solution under visible light via a simple method. TiO₂ P25 was used as the base photocatalyst because of its good photocatalytic activity. Semnan natural zeolite (SNZ) was the adsorbent of choice due to its good adsorption property and availability at an affordable cost. A pharmaceutical capsule was used because of its similarity to an actual waste water sample.

2. Materials and methods

2.1. Materials and chemicals

Titanium dioxide P25 (80% anatase and 20% rutile) was supplied by Evonik industries. Semnan natural zeolite tuffs were obtained from the Semnan region in the north-east of Iran. The TC ($C_{20}H_{24}N_2O_8$) pharmaceutical 250 mg capsule was obtained from the Iran Daru Company. Distilled water was used throughout the experiments.

2.2. Preparation of TiO₂/SNZ nanocomposite

To prepare the mixed photocatalyst, SNZ and TiO_2 P25 were mixed mechanically. In a typical preparation of the supported

photocatalyst, TiO₂ P25 (1 g) was mixed with 5 g of SNZ in powder form and added to 60.0 mL of deionized water at room temperature. The mixture was stirred and ultra-sonicated for 60 min. The solid was collected and washed by deionized water and then dried under 100 °C for one night in an oven. Finally, the solid was calcined at 450 °C for 8 h. Figure 1 shows the commercial TiO₂ P25 and as-prepared TiO₂ supported on SNZ.



Fig. 1. Photo of a) Commercial TiO₂ P25, b) as-prepared TiO₂/SNZ nanocomposite

2.3. Analysis and characterization methods

The structure of the commercial TiO₂ P25, natural zeolite, and TiO₂/SNZ was examined by using a diffractometer Bruker, D8 (with X-ray tube anode and Cu K_{α} wavelength: 1.5406 Å). The surface morphology of the samples was studied using a KYKY-EM-3200 scanning electron microscope (SEM). The BET surface areas of the samples were determined from the isotherm data of the nitrogen adsorption data in the relative pressure (P/P₀) range of 0.05–0.30 obtained at 77.35 K using a Quanta chrome Autosorb-1 analyzer. The UV–Vis spectra were obtained on a Shimadzu UV-1650PC spectrophotometer. Fourier transform-infrared spectroscopy (FTIR) in the range of 400-4000 cm⁻¹ was recorded (Shimadzo FT-IR 8400S).

2.4. Photocatalytic degradation experiments

A photocatalytic reactor with two lamps of 60 Watt as the visible irradiation source was used to degrade the TC as a pollutant (Figure 2). To prepare the TC solution, the contents of a 250 mg capsule was dissolved in water and shaken for 30 min; then it was filtered in a 100 mL volumetric flask and diluted with water. The photoreactor was filled with 300 ml of 8 mg/L pollutant and 0.8 g/L of photocatalyst at an irradiation time of 90 min. The whole reactor was cooled with a watercooled jacket on its outside, and the temperature was kept at 25°C. In order to set the adsorption/desorption equilibrium of the pollutant on a heterogeneous catalysts surface, the reactor was kept under dark conditions for 30 min. An aliquot suspension was withdrawn and centrifuged at 5000 rpm to remove the solid particles. The UV-Vis absorption spectra of the TC solution was scanned and showed an optimum band centered at 360 nm, which can be used as the absorbance wavelength for the establishment of the TC standard curve by the principle of the Lambert-Beer law. The concentrations of different TC samples could be measured from the standard

curve. The degradation extent was calculated according to the following formula based on the absorbance of the solution (at λ_{max} = 360 nm) before and after irradiation.

TC degradation % =
$$[(C_0-C_t)/C_0] * 100 = [(A_0-A_t)/A_0] * 100$$
 (1)

Where C_0 and C_t are the initial and final concentration of TC at time t, respectively. A_0 and A_t are respectively the initial and final absorbance of the samples. The absorbance values were used to calculate the percent of degradation.



Fig. 2. Schematic diagram of the home-made photo reactor

3. Results and discussion

3.1. TiO₂/SNZ nanocomposite characteristics

3.1.1. XRD analysis

In order to confirm the structure and crystallinity of the TiO₂/SNZ catalyst, an XRD study was carried out. The XRD patterns of natural zeolite and TiO₂/SNZ nanocomposite were recorded and are shown in Figure 3 for comparative purposes, the diffraction pattern of commercial TiO₂ P25 was also included. The presented results revealed that the SNZ particles used were mostly Clinoptilolite (CP) $(2\theta=11; 22.5; 30)$ [6, 19]. There was no significant shift of the zeolite in the TiO₂/SNZ peaks by comparison with those of pure zeolite; however, the intensity for the SNZ peaks was lower when compared to the natural zeolite particles. This suggested that the TiO₂ precursor interacted with the support, decreasing the crystallinity of the SNZ. This was in good agreement with other research [17]. It can be seen from Figure 3 that the main peak positions of natural zeolite were remarkably unchanged, indicating that the structure of natural zeolite had good thermal stability. This also revealed that most of the TiO₂ was distributed on the surface of natural zeolite while a part was encapsulated in the cavities.

A similar XRD pattern was obtained for TiO₂ loaded on natural zeolite as reported previously [20-22].



Fig. 3. XRD Spectra of a) Commercial TiO $_2$ p25, b) SNZ particles c) as-prepared TiO $_2$ /SNZ nanocomposite

The characteristic diffraction peaks of TiO₂ P25 can be observed at 2ϑ =25.4 corresponding to the (101) plane of anatase, indicating that TiO₂ has been impregnated within the sample. A small portion of rutile was also observed in the TiO₂ sample as the appearance of the peak at 2ϑ =27.8 corresponding to (110) plane of rutile, which was overlapped with those of the Semnan natural zeolite [23]. No peaks of impurities were detected, indicating the high phase purity of the as-prepared sample. The average crystallite size of the commercial TiO₂ P25 and TiO₂/SNZ was calculated using the Scherrer equation to be about 21.6 and 27 nm, respectively.

3.1.2. SEM surface morphology

The morphology of the SNZ and TiO₂ supported on SNZ was investigated using SEM, as illustrated in Figure 4. It shows the SEM images of the SNZ surface before and after coating with the TiO₂ P25. The SEM results were also in agreement with XRD as there was no major change in the structure of the SNZ. Also, the surface grain of SNZ was much smoother than that of the TiO₂/SNZ. The TiO₂ spherical nanoparticles (size 30 nm) were present as clusters attached to the zeolite matrix of the modified SNZ. Collectively, these images supported the conclusion that TiO₂ was well dispersed on the external surface of SNZ. It could also be seen that the TiO₂ coating was relatively uniform and there were no apparent sites of uncoated zeolite. Figure 4 also shows pore openings and cavities resulting in an

increased specific surface area of the composite, thus providing higher adsorption sites for contaminant adsorption. These findings were consistent with other research [11, 17, 24].



(a)



(b)

Fig. 4. SEM images of (a) SNZ particles, (b) as-prepared TiO₂/SNZ nanocomposite

3.1.3. Specific surface area

The surface area (S_{BET}) of the samples was determined from the N2 adsorption-desorption isotherms using the Brunner-Emmet-Teller method. The BET specific surface area of the TiO₂ and synthesized composite were measured to be 50 and 93 $m^{2/}g$, respectively. The increase in the surface area after modification resulted from the distribution of TiO₂ throughout the natural zeolite matrix. As the pore size of the zeolite was smaller than the size of the TiO₂ particles supported by the zeolite, the TiO₂ particles were coated on the zeolite surface and not on the inside of the internal pores of the zeolite. In other words, the pore diameter for the zeolite was considered to be too small for TiO₂, and therefore during the preparation of zeolite/TiO₂, the sorption of TiO₂ on natural zeolite was limited to the sites on the external surface. Surface area measurement disclosed an enhancement of surface area by ~2 times for the synthesized TiO₂/SNZ than that of the commercial TiO₂ P25, which rendered SNZ as an ideal support for TiO₂. The high surface area enabled TiO₂/SNZ to simplify the adsorption of TC (model pollutant) on the catalyst and improved the photocatalytic activity of the catalyst with respect to TC degradation.

3.1.4. UV-vis DRS

The UV-vis diffuse reflectance spectroscopy (DRS) was used to analyze the optical properties of catalyst and is depicted in Figure 5. Clearly, the TiO₂/SNZ catalyst was able to well absorb both the UV and visible light. It can be seen that the TiO₂/SNZ sample, unlike the commercial TiO₂ P25, showed absorbance in the visible range which suggested its potential to be activated by visible light. The determination of the band gap from the UV-vis spectra was an alternative method to study the modification of the electronic property of the synthesized species. The energy band structure was a key factor affecting the photocatalytic activity of catalysts [25]. The band gap of the composite was estimated by Tauc's equation using the absorption data:

$\alpha = \alpha_0 (hv - E_g)^n / hv$

where α is absorption coefficient, α_0 and h are the constants, hv is the photon energy, E_g is the optical band gap of the material, and n depends on the type of electronic transition and can have any value between 0.5 and 3. The energy gap of the sample (Eg) has been distinguished by extrapolating the linear portion of the plots of $(\alpha hv)^{0.5}$ against hv to the energy axis.



Fig. 5. UV–Vis diffuse reflectance spectra of commercial TiO₂ P25 and TiO₂/SNZ sample (inset: estimated band gap of TiO₂/SNZ)

The valence band (VB) and conduction band (CB) potentials of the semiconductor at the point of zero charge can be calculated by the following formula:

$E_{VB}=X-E^{c}+0.5E_{g}$

where E_{VB} or E_{CB} are the VB or CB edge potentials of semiconductor, respectively, X is the absolute electronegativity of its constituent atoms, E^c is the energy of free electrons on the hydrogen scale (ca. 4.5 eV), and E_g is the band gap of semiconductor. The CB position can be calculated by $E_{CB}=E_{VB}-E_{g}$ [26]. Since zeolites generally do not absorb any light in UV-vis regions, they are one of the most suitable supports for photocatalysis. The results revealed a clear trend in decreasing the band gap of commercial TiO₂ P25 from 3.2 to 2.4 eV for TiO₂ supported on SNZ. This suggested that the particle size of TiO₂ supported on zeolite was larger than that of commercial TiO₂ used in the present study (quantum size effect) [27, 28]. Furthermore, zeolite delocalizes the band-gap excited electrons of TiO₂, thereby minimizing electron/hole recombination.

3.1.5. FTIR spectroscopy results

Figure 6 presents the FTIR spectrum of TiO₂/SNZ in comparison with SNZ to demonstrate the possible bonds of TiO₂ with the natural zeolite. The strongest absorption peak at 1047 cm⁻¹ was assigned to the framework stretching vibration band of Si (AI)-O in natural zeolite, its position was unchanged at a 450 °C treatment temperature, indicating that the zeolite structure was not destroyed at 450 °C. Also, the adsorption bands of TiO₂/SNZ were mostly similar to those of SNZ. This indicated that SNZ was highly suitable to act as a TiO₂ P25 immobilizer, as the structure was not affected by the high annealing temperatures used. The infrared analysis confirmed that the TiO₂ P25 particles combined with the active sites of SNZ and Ti-O-Al and Ti-O- Si which make up the load of TiO₂ P25. A new absorption band was found in the spectra of TiO₂/SNZ comparable with the SNZ. The band covered a range from 945 to 900 cm⁻¹ corresponding to the stretching vibration of Ti–O– Si and Ti–O–Al, which was similar to the results of Li et al. [29].



Fig. 6. Comparison of the FTIR spectra of pure SNZ and TiO₂/SNZ nanocomposite

3.2. Photocatalytic degradation of TC

The influence of pH on the photocatalytic degradation extent of TC by supported TiO_2 onto SNZ (TiO_2/SNZ) was evaluated by varying the initial pH of the TC solution and keeping all other experimental conditions constant. In order to compare the degradation efficiency, some reaction was carried out with initial acidic pH and alkaline pH in the range of 4-10. The effect of pH on the photocatalytic reaction was generally attributed to the surface charge of the catalyst and its relation with the ionic form of the organic compound (anionic or cationic). Electrostatic attraction or repulsion between the surface of the catalyst and the organic molecule took place and consequently enhanced or inhibited, respectively, the photodegradation rate. The photocatalytic degradation efficiencies of TC under visible light by TiO₂/SNZ were obtained in the order of pH 6 > pH 10 > pH 8 > pH 4. Further, 87% of TC was photodegraded at a pH of 6 after 90 min, while only 10% of TC was removed at a pH of 4 under the same experimental condition. The point of zero charge (pzc) of TiO₂/SNZ, i.e., the point when the surface charge density is zero, was found to be of 7 and is shown in Figure. 7. This value corresponded to the pH at which the straight line (pH_{initial} = pH_{final}) crossed the sigmoid curve passing through the experimental points [30].



Fig. 7. (a) pH_{PZC} of TiO₂/SNZ, (b) Effect of pH on TC photocatalytic degradation by TiO₂/SNZ under visible light

The electric charge properties of both the catalyst and substrate were found to play an important role on the adsorption process. The surface of the catalyst was positively charged at a pH < pH_{pzc}, negatively charged at a pH > pH_{pzc}, and remained neutral at a pH = pH_{pzc}. Such behavior significantly affected not only the adsorption-desorption properties of catalyst surface, but also the changes of the pollutant structure at various pH values. In addition, the pKa1, pKa2 and pKa3 values of the TC molecule are 3.3, 7.68, and 9.7, respectively, which are related to equilibriums (TCH₃⁺ \rightarrow TCH₂, TCH₂ \rightarrow TCH⁻, and TCH^{- \rightarrow}TC₂⁻). The adsorption mode and the concentration of OH were two key factors influencing the photocatalytic degradation efficiencies of TC at different pH values [4]. The pH_{PZC} of the synthesized catalyst was found to be about 7. The adsorption of TC on the catalyst might be inhibited by the enhanced electrostatic repulsion between H₃TC⁺ and the positively charged catalyst at a pH of 4 as well as between HTC⁻ $/TC_2^-$ and a negatively charged catalyst at a pH of 8 and 10, respectively. Also, in a pH =6, the TCH⁻ and TC₂⁻ species were dominant and the surface of the nano composite particles had a positive charge. Thus, the TC molecule seemed to be attracted to the positively charged TiO₂/SNZ surface. Furthermore, the decrease of the reaction rate at acid pH can

be ascribed to the lower hydroxylation of the catalyst's surface due to the presence of small amounts of OH⁻ ions. To assure of the removal of TC by photocatalytic degradation, several control experiments were investigated and are shown in Figure 8. It clearly indicated that the TC could hardly be degraded without any photocatalyst (photolysis) while the TiO₂/SNZ nanocomposite showed a much higher activity than the TiO₂ (alone) with visible light exposure. Also, the removal of TC by adsorption on the SNZ was not comparable by photocatalytic degradation of TC on the TiO₂/SNZ. After irradiation for 90 min, only 25% TC removal over the SNZ was observed, while the removal ratio on the TiO₂/SNZ reached 87%. The degradation of TC by commercial TiO₂ P25 under visible light did not occur, due to the inability of the absorption of visible light.



Fig. 8. Degradation of TC in the solution with initial concentration of 8 mg/L under visible light irradiation

4. Conclusions

TiO₂ supported on SNZ was successfully synthesized by employing a facile method. The results of this study suggested that the surface immobilization of TiO2 onto SNZ can enhance its surface area and its ability to activate under visible light. The photocatalytic activities of the catalysts were studied by measuring the photodegradation of the TC solution. The catalysts showed pH dependence and more than 87% of the TC could be removed from the solution within 90 min at a pH of 6. In addition, the immobilization of TiO₂ onto zeolite particles permitted for easier separation of the adsorbent (compared to finer nanoparticles of TiO₂) from the treated water. Diffuse reflectance spectroscopy revealed a clear trend of decreasing the band gap to 2.4 eV when TiO₂ was supported on SNZ. The specific surface area for the composited material reached 93m²/g, which was two times larger than the unmodified TiO2. With these improvements, the TiO₂/SNZ was able to absorb more pollutant because of a higher surface area and enhanced visible light absorption rather than commercial TiO₂ P25. The finding of this study could benefit future applications in water and wastewater treatment.

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