Preparation and Photocatalytic Characterization of Modified TiO2/Nd/rice Husk Ash Nanomaterial for Rifampicin Removal in Aqueous Solution

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Preparation and photocatalytic characterization of modified TiO_2/Nd/rice husk ash nanomaterial for Rifampicin removal in aqueous solution

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Abstract

The neodymium doping of titanium dioxide with content of Nd varying from 0.01 to 0.8% was conducted by the sol-gel hydrothermic method. TiO_2/Nd is then coated on rice husk ash to produce modified TiO_2/Nd/rice husk ash material using Nd content of 0.36% w/w. The materials' structure characteristic and photocatalytic properties have been analyzed by the XRD, EDX, TEM, SEM, forbidden zone energy (Eg) and specific surface area (BET). TiO_2/Nd material shows a higher photocatalytic decomposition capacity in comparison to TiO_2 and depended on the Nd content. The Rifampicin removal efficiency of TiO_2/Nd materials with Nd contents ranged from 0.36 to 0.80% had an increase of about 40% higher than that of TiO_2/Nd containing Nd from 0.01 to 0.28%. This new photocatalytic TiO_2/Nd/rice husk ash material is used to decompose Rifampicin. Within 90 minutes under sunlight, the Rifampicin decomposed efficiency of TiO_2/Nd and TiO_2/Nd/rice husk ash material reached about 86 and 75%, respectively. Even lower efficiency was obtained, the latter material was chosen for Rifampicin residue decomposition in the water under sunlight through photocatalytic process because it has some advantages such as smaller amount was needed and easily to be recovered. Rifampicin removal process, k values were found matching more to zero and first order kinetics. Especially, for powder TiO_2/Nd and TiO_2/Nd/Rice husk ash under solar irradiation the R^2 reached about 0.98.

Introduction

Rifampicin is an antibiotic with the molecular formula $C_{43}H_{58}N_4O_{12}$ that works with bacteria of the Mycobacterium strain, especially *M. tuberculosis, M. leprae* and other Mycobacterium bacteria such as *M. bovis, M. avium*. The minimum inhibitory concentration for *M. tuberculosis* bacteria are 0.1 - 2.0 micrograms/ml. The presence of particular antibiotics especially Rifampicin in water has a significant influence on water treatment by biological methods.

The removal of antibiotic residues has been of great interest to many scientists. Currently, there are many methods of antibiotic residues removal such as absorption, advanced oxidation, biology, photocatalyst etc. Using photocatalyst is one of the techniques that promises to decompose not only persistent organic pollutants (POPs) that are difficult to decompose by biological methods, harmful microorganisms, but also, remove some antibiotics that are difficult

or impossible to treat by biological methods etc. The characteristic of this type of catalyst is that, under the effect of light, will produce pairs of electrons (e^-) and hole (h^+), thereby creating compounds with strong oxidation properties and abundant electronic supplies (Choi, Maruthamuthu et al. 2009, Yang, Doudrick et al. 2013, Saucedo-Lucero and Arriaga 2015, Hajizadeh, Amin et al. 2018).

Nano TiO_2 has widely used because of its photochemically stable, photocatalytic property, low cost and nontoxic to human and environment. Nano TiO_2 that is used as catalyst will not be converted by reactions, therefore, it is required only initial investment for long term use (Wen, Li et al. 2015, Huang, Lu et al. 2017, Aregu, Asfaw et al. 2018). Therefore, nano-size TiO_2 has the economical and technical advantages in inorganic, organic or microbials removal (Aregu, Asfaw et al. 2018). However, due to restricted zone energy of nano-size TiO_2 is high (3,05−3,25 eV), only the short wavelength radiation (< 380 nm) could activate the electron from the valence to the conduction bands for photocatalytic activity (Ma, Wang et al. 2014, Wen, Li et al. 2015). Mean whiles, the ultraviolet radiation in the solar radiation reaches the Earth's surface only account about 4 %, making the use of this natural source for the purpose of treating environmental problems with TiO_2 is limited (Li, Yu et al. 2015, Wen, Li et al. 2015). Therefore, it is necessary to reduce the band-gap energy of TiO_2 so it has photocatalytic activity under the visible light. As a result, many researches have denatured TiO_2 materials to narrow down the bending energy (Eg), to enlarge the excitation light from the UV region to the visible area (Ma, Wang et al. 2014, Li, Yu et al. 2015, Wen, Li et al. 2015).

Number of the recent surface modifications or TiO_2 structures by various methods have been carried out by introducing metal ions such as Zn, Fe, Cr, Eu, Y, Ag, Ni, etc. and non-metal ions such as N, C, S, F, Cl,.... These materials have been shown to be effective, enhancing photocatalytic activity in the visible light region (Chen and Mao 2007, Maeda and Domen 2007, Du and Eisenberg 2012, Fukuzumi, Hong et al. 2013, Wanga and Astruc 2014, Li, Yu et al. 2015, Wen, Li et al. 2015).

In addition, due to small and dispersion the TiO_2 nanoparticles is difficult to recover for reuse. Therefore, to reduce the cost of products needs to attach TiO_2 nanostats to the carrier has a large surface area. These carriers should have the following characteristics: good bonding to the catalyst; no catalytic decomposition effect; has a large surface area; has an affinity for adsorption

with pollutants such as beeswax, activated carbon, glass, silica gel, polymer materials, zeolite, cotton, cellulose…

Husk cover and rice husk ash are agricultural waste, accounting for about one fifth of the world's annual production of rice (about 545 million tons per annum). Globally, there are more than twenty million tons of husk ash released each year (General statistics office 2018). The amount of ash that enters the ecosystem can be damaging to humans and animals, such as silicosis, respiratory failure, and death. Husk ash is used as a good adsorbent for the treatment of many inorganic and organic pollutants (Liu, Guo et al. 2011, Kumar, Sengupta et al. 2015, Zhang, Ding et al. 2015). Therefore, solves a part of agricultural waste, reducing the amount of waste rice husk (Liu, Guo et al. 2011). In addition, husk ash is also used as a carrier for catalytic materials because it has a good mechanical stability, are chemically inert, when used as a carrier will facilitate the separation of catalyst from the solution after reaction. The application of this material is that absorbing nitrogen compounds like Rifampicin (Kumar, Singha et al. 2015).

Thus, utilizing rice husk ash and adsorbents of nitrogen - containing organic compounds such as Rifampicin, coupled with photochemical capacities of TiO_2 nanoparticles photochemical catalysts for the transfer of Rifampicin to CO_2, H_2O, N_2 (non-toxic). One that solves the problem of minimizing environmental pollution from agricultural waste, on the other hand increases the efficiency of nanomaterials as well as saves on materials and does not require post-processing solutions. It opens up a new way of handling nitrogen compounds as well as can be applied in industry (Cong, Zhang et al. 2007).

Experiment

Chemicals and equipment

Chemicals used in research include: $TiCl_4$, NH_4NO_3, PVA, $(NH_2)_2CO$, Rifampicin (see Figure 1), Methanol, H_2SO_4, HNO_3, Na_2CO_3, NaOH, NaH_2PO_4, Na_2HPO_4, $NdCl_3$. The chemical compounds have a purity of PA, produced by the Merck, German, distilled water and super distilled water.

Figure 1. The chemical structure of Rifampicin

Husk is taken from the Rice enterprise in Hoai Duc, Ha Noi. The rice husk is washed with distilled water to remove impurities, dried at 105°C for 2 hrs., then put in furnace at temperatures of 800°C for 3 hrs. in N_2 gas environment to have ash bearing material. The product after furnace is grinded to the size of about 0.1-0.5 mm.

Water samples: water sample containing Rifampicin is prepared with Rifampicin concentration 20 mg/L. $TiCl_4$ 0.5M was prepared from $TiCl_4$ 3M by diluted using cold water.

Buffer solution of phosphate pH 7.4 is prepared from the NaH_2PO_4 and Na_2HPO_4.

Instruments were used to perform experiments consist of: Drying cabinet produced by Germany; oven Carbolite model AAF-11/7 produced in England. Heating magnetic stirrer IKA by Germany.

Preparation of modified TiO_2/Nd nanomaterial coated in husk ash by the sol-gel hydrothermal method

Preparation of modified TiO_2/Nd nanomaterial by the sol-gel hydrothermal method

TiO_2 nanomaterial modified Nd was prepared by the sol-gel hydrothermal method according to Nguyen H.N. et al (2016): Mixing 60 ml NH_4NO_3 1M with 450 ml $(NH_2)_2CO$ 1M + 180 ml PVA 1M + 60ml $TiCl_4$ (0,5M) + from 0.1 to 1.0 ml (1g/L); heating to 70°C, stirring continuously in 24 hrs., 1200 rpm, then heating up to 90°C, and stirring for 12 hrs. Sol-gel solution obtained was dried at 120°C for 12 hrs., then the temperature was increased to 250°C for 3 hrs. until no more white smoke was released, and black powder was generated. Finally, materials were put in furnace at 600ºC for 3 hrs. with a heating rate of 10°C/min. Materials after the furnace were washed 4-5 times with distilled water and super clean water, then dried at 120°C for 2 hrs (Nam, Hiep et al. 2016).

Table 1. Composition and rate of chemicals prepared nano TiO_2 modified Nd by the sol-gel hydrothermal method

Coating TiO_2/Nd nanomaterial on rice husk ash

Husk ash was added into sol-gel solution prepared in section 2.2.(a) to have the concentrations of TiO_2/Nd in husk ash corresponding 0.1; 0.2; 0.3; 0.4 and 0.5% w/w. The thermal modification process started with well stirring the mixture at 90°C for 12 hrs. then was followed by similar processes as in the preparation of Nd modified TiO_2 nano-materials in section "*Preparation of modified TiO_2/Nd nanomaterial by the sol-gel hydrothermal method".*

Rifampicin removal of TiO_2/Nd nanomaterial and TiO_2/Nd nanomaterial/husk ash

Put 0.1g of powdered TiO_2/Nd nano-material or 1.0g TiO_2/Nd nanomaterial/husk ash in 200ml glass cups, add 100 ml of Rifampicin solution at 20 mg/L, stirring the solution at 100 rpm. Experiments were conducted under natural light (day and night). The natural light has illumination

intensity of 20.000 Lux. Samples were taken at 0, 15, 30, 45, 60, 75 and 90 minutes to analyze residual Rifampicin concentration.

Analysis methods

The surface area of the husk ash is determined by the BET analysis in N_2 environment at 196°C using NOVA 1200 Quanta chrome-USA. Surface structure of husk ash and TiO_2 material/husk ash defined by the SEM method (Jeol 5410 LV, Japan). Purity of a TiO_2 material defined by X-ray diffraction method (XRD), Siemens D5005, Germany. Nano TiO_2 particle size determined by TEM, LIBRA120, Germany. The element compositions are analyzed by Energy dispersive analysis of X-rays (EDX), Jeol 6490JED 2300, 2300, Japan.

Rifampicin concentration was analyzed by molecular absorption spectrospic method according to Benetton et al. (1998). Calibration curve was prepared using UV-VIS Optizen 2120UV, England.

Rifampicin degradation kinetic calculations

The rate of rifampicin degradation and observe the best fit indicating the reaction order were investigated by plotting the remained rifampicin concentration versus time using zero-order, first-order and second-order kinetic models (Vaucher, Paim et al. 2010):

Zero-order reaction: $C = C_0 - kt$ (1)

First-order reaction: $C = \ln C_0 - kt \rightarrow C = C_0 e^{-kt}$ (2)

Second-order reaction: $\frac{1}{C} = \frac{1}{C_0} + kt\frac{1}{C}$ (3)

Where*:* C_0 is the concentration of the reactants under consideration at time zero; C is the concentration after reaction time, t; k is the reaction rate constant.

Based on the obtained kinetic graphs, regression coefficients and the kinetics parameters such as apparent order degradation rate constant (k) were identified.

Results and discusions

Characteristics of powder TiO_2/Nd modified material

Samples of TiO_2/Nd material obtained after synthesis with different Nd contents were analyzed the structure, photolysis properties and surface properties using of EDX, XRD, SEM,... measurements.

Ermology of nano TiO_2/Nd modified material

To analyze the size of the prepared material and their crystal forms, conduct particle size analysis using TEM and XRD. The ermology of the nano TiO_2/Nd modified materials using the solgel hydrothermical method is shown on Figure 2.

Figure 2. TEM image of TiO_2/Nd modified nanomaterials with different Nd content

Figure 2 shows that, with different Nd content the materials are even in the form of anatase and has a relatively even particle size, at about <20 nm. Compared to the results of the synthesis of nano materials by the solgel method (Nam, Hiep et al. 2016), the nano TiO_2/Nd modified materials have the particle sizes more even and smaller than that of non-modified materials. This result is also consistent with the findings of the study by Huang You et al (2006) and Nam et al. (2016).

The XRD spectrum of the TiO_2/Nd modified nanomaterials

X-ray diffraction (XRD) patterns of the nano TiO2 non-modified materials and the nano TiO2/Nd modified materials are shown on Figure 3. As can be seen all peaks are sharp and no strange diffraction peaks appeared that prove the prepared TiO2 materials have a characteristic crystal structure. Diffraction peaks are characteristic at 2θ values about 25.36 (101), 37.93 (004), 48.07 (200), 5 4.03 (105), 55.13 (211) and 62.81 (204) show that the nano materials obtained exist only in the anatase phase. In addition, no characteristic peaks of the rutle and brookite phase appear.

Figure 3. XRD images of nano TiO_2/Nd modified materials with different Nd content

Table 2. Lattice parameters, particle size and density of *TiO_2/Nd* modified nanomaterials with different Nd content

The results showed that Nd^{3+} ions were inserted in the crystal structure of nano TiO_2 materials. Although they are prepared with different Nd contents, the nano materials obtained are pure, single-phase, without the appearance of diffraction peaks of rare earth ions. Besides, the crystal lattice parameters of materials with different Nd contents there are differences in lattice constants a and c, in which of nano TiO_2/Nd modified material found larger sizes than non-modified materials. This can be explained, since the radius of the Nd^{3+} ion is larger in size than that of the Ti^{4+} ion, when the Nd^{3+} ion replaces the position of the Ti^{4+} ion in the crystal lattice it will make the crystal larger in size (El-Bahy, Ismail et al. 2009, Nguyễn Văn Hưng, Ngô Sỹ Lương et al. 2012).

However, the size of the crystal lattice and the density of all 6 materials are almost the same. In addition, these findings are similar to some previous studies where the lattice cell size of the material prepared by the sol-gel hydrothermical method is smaller and the density is larger when modifying by metals (Huang, You et al. 2006, El-Bahy, Ismail et al. 2009, Nguyễn Văn Hưng, Ngô Sỹ Lương et al. 2012).

EDX spectrum of TiO_2/Nd nanomaterials

The percentages of elements contained in nano TiO_2/Nd materials with different contents of Nd are in shown in Figure 4.

Figure 4. EDX images of TiO_2/Nd modified nanomaterials with different Nd contents

Peaks on EDX diagrams specify the presence Ti, O and Nd elements in material samples. Peaks of other elements are not appeared. This proves that synthetic TiO_2 nanomaterials are highly pure. The results of quantitative analysis of the material's compositions show that Ti content accounts for between 46 and 57% by weight and from 27 to 31% by atomic numbers, O content found in the ranges of 42-54% and 69- 78% by weight and atomic numbers, respectively. Except Ti and O peaks, there was peaks of Nd, with a relatively small intensity, accounting for only 0.01 to 0.8% and from 0.01 to 0.14 % by weight and atomic number, respectively.

Nano materials are obtained evenly in single-crystal form and in the form of anatase. In the crystal lattice of TiO_2, Ti atoms in some vertices are replaced by Nd atoms. However, since Ti has valency IV, it will form a bond with the 4 surrounding O atoms while the Nd has valency III, so when Nd is replaced in the position of the Ti atom, the Nd atom creates a electric imbalance. In addition, on the surface of TiO_2 there are OH^- groups that produce from water separation process of oxides. These groups can exist in a free or the surface bond states through hydrogen bonds. That's why the TiO_2 surface form several molecular layers. The OH^- group can catch holes and absorbed water molecules that can give electrons to form reduced hydroxyl radicals. Therefore, the rate of re-combination between electron-hole pairs is reduced and the photocatalytic activity of TiO_2 is enhanced when it is modified by the Nd^{3+} ion (El-Bahy, Ismail et al. 2009).

Eg values of TiO_2/Nd modified nanomaterial

As can be seen in Figure 5, the sample has an Nd content of 0.16% for the lowest Eg value. The highest Eg value found at material with an Nd content of 0.8%, reaching 3.21 eV. Thus, when modified by Nd, generally the forbidden zone energy of the material is lower in comparison to non-modified one. That shows the ability to absorb the visible light of these modified materials is

greatly improved compared to nano TiO_2 material. For non-modified TiO_2, maximum energy absorption takes place in the ultraviolet radiation region ($\lambda < 400$ nm) with electron excitation from orbital 2p of the O atom the orbital 3d of Ti. Therefore, the Eg value of TiO_2/Nd materials with different Nd contents significantly decreases to below 2.89 eV. As a result, visible light can excite electrons from this intermediate energy level (4f) to the conductive region energy. This is also agreement with the studies on TO_2 modified using rare earth elements (Wojcieszak, Kaczmarek et al. 2012, Wojcieszak, Mazur et al. 2014).

Figure 5. Eg spectrum of TiO_2/Nd modified nanomaterials with different Nd contents

TiO_2/Nd nanomaterials coated on rice husk ash

The nano TiO_2/Nd modified materials coated on rice husk ash are prepared from sol-gel solution similar to those used to make nano TiO_2/Nd modified materials with a content of 0.36% Nd. Their photocatalytic activity is compared to nano TiO_2 particles. The SEM image of the nano TiO_2/Nd /rice husk ash material shows that on the surface of the material at the crevices and on the holes, there are nano TiO_2/Nd particles that are attached and they are fairly evenly distributed throughout the surface of the rice husk ash. The results also indicate that the coatings on the rice husk ash are homogeneity (see Figure 6).

Figure 6. SEM images of rice husk ash (a) and nano TiO_2/Nd /rice husk ash (b)

Figure 7. XRD (a) and EDX (b) spectrum of nano TiO_2/Nd /rice husk ash

Figure 7 (a) shows the characterized peaks appeared at the 2θ position = 25.3º of TiO_2, and 22º of SiO_2 that indicate the presence of TiO_2 and SiO_2 particles on the surface of nano TiO_2/Nd /rice husk ash material. Mass and percentage of elements found in nano TiO_2/Nd/rice husk ash material are presented in Figure 6 (b). The findings show that the material consists mainly of Si, accounting 83.13%, the O and C make up 6.33 And 5.64%, respectively. However, Ti only occupies a small amount (0.19% w/w), where a small amount of other elements like Nd, K, Cl and Ca are found to derive from rice husk ash. It shows that nano TiO_2/Nd coating rice husk ash material by solgel hydrothermal method has been achieved successfully because of high absorption capacity and photocatalytic activity. Using this material makes the continuous operation of the treatment processing without separating the material after treatment. In addition, it not only increases the removal efficiency but also reduces the treatment cost.

Removal effective of rifampicin of Nd-TiO_2 and Nd-TiO_2/rice husk ash nanomaterials

The result of photocatalytic decomposition of the rifampicin antibiotic in the presence of TiO_2/Nd and TiO_2/Nd/rice husk ash nanomaterials show in Figure 8. The results clearly show that both types of materials obtained have photocatalytic activity. However, the activity of TiO_2/Nd /rice husk ash material is lower (about 10% after 90 min), compared to the decomposition of rifampicin antibiotics obtained in the case of nano TiO_2/Nd material. This difference is mainly related to significant differences in the content of nano TiO_2, the light absorption ability, the rifampicin's absorption capacity onto the rice husk ash material. Although, both materials are prepared from same size nanoparticles and having the same Eg, the BET surface areas of nano TiO_2/Nd and TiO_2/Nd/rice husk ash materials are 58.97 and 107 m^2/g, respectively. The size of the TiO_2/Nd /rice husk ash is also much larger than the size of the nano TiO_2/Nd particle. Because of the bulky molecular structure of rifampicin with many functional groups such as -OH, >NH, >C=O etc., it can easily make bonds with the metals of the adsorbents. This show more clearly in the experiment results under the dark conditions (see Figure 8). Also, the very fast absorption rate can be seen that maximum absorbability is achieved after 15 minutes.

Under natural light conditions, the photocatalytic efficiency of both materials increases markedly over reaction times. However, the rifampicin decomposition efficiency of nano TiO_2/Nd particles is higher. This is related to the absorption process as well as the size of the rifampicin molecule. Therefore, the photocatalytic process takes place simultaneously during absorption as below reactions (Thomas, Radhika et al. 2016).

$$TiO_2 + hv \rightarrow TiO_2\ (h^+ + e^-) \quad (4)$$

$$TiO_2(h^+) + H_2O \rightarrow {}^{\cdot *}OH + H^+ + TiO_2 \quad (5)$$

$$TiO_2(h^+) + OH^- \rightarrow {}^{\cdot *}OH + TiO_2 \quad (6)$$

$$TiO_2(h^+) + O_2 \rightarrow {}^*O_2 + TiO_2 \quad (7)$$

The activated molecules formed will react with the molecules of rifampicin to produce CO_2 and H_2O.

$$C_{43}H_{58}N_4O_{12} + 103/2({}^*O_2) \rightarrow 43CO_2 + 29H_2O + 2N_2 \quad (8)$$

$$C_{43}H_{58}N_4O_{12} + 194({}^*OH) \rightarrow 43CO_2 + 66H_2O + 2N_2 \quad (9)$$

From the reaction equation, a large number of activated molecules are needed to oxidize the $C_{43}H_{58}N_4O_{12}$, which means a large amount of h^+ is needed for the reaction.

Figure 8. Rifampicin removal efficiency of nano TiO_2/Nd and TiO_2/Nd /rice husk ash under different conditions (TiO_2/Nd-P: nano TiO_2/Nd, natural light; TiO_2/Nd/H-SL:TiO_2/Nd/rice husk ash, natural light; TiO_2/Nd/H-D: TiO_2/Nd /rice husk ash, dark)

At an early stage, when Rifampicin molecules are quickly adsorbed to the surface of material, it prevents OH^- ion and O_2 molecular interact with the material surface, thereby reducing the formation of activated molecules and facilitating the re-combination of e and hole. Therefore, the rifampicin removal efficiency through photochemical reaction is insignificant. As the reaction time is prolonged, the rates of photochemical reaction of both materials markedly increases. The concentration of rifampicin tends to decrease more significantly for nano TiO_2/Nd materials in comparison to TiO_2/Nd/rice husk ash. This is probably because the rice husk ash accounts for a large proportion of the TiO_2/Nd/rice husk ash material (see SEM and EDX).

In the later material, nano TiO_2/Nd particles occupy only a small part of the surface area of the material, therefore, when the rifampicin molecules are absorbed onto the rice husk ash material, the interact between the activated molecules and rifampicin has a lower probability than the nano TiO_2/Nd material. On the other hand, due to the larger size of the TiO_2/Nd/rice husk ash material, it prevents light from going deep into the solution, so the decomposition efficiency is lower and the reaction time lasts longer. When the reaction time lasts up to 90 min, the rifampicin decomposition efficiency of TiO_2/Nd/rice husk ash material reaches about >75%.

Rifampicin degradation kinetics

The results of the kinetic calculations relating to the process of removing rifampicin according to the zero, first and second equations were showed in Figure 9.

Summarized results in Table 3 showing that for all 3 kinetics the powder TiO_2/Nd has the highest k-value and regressive correlation, R^2. The k value in zero kinetic and 1^{st} order kinetics are similar to the maximum and minimum k values, respectively, that were reported in the study of Cizmic et al. (2019) (Cizmic, Ljubas et al. 2019).

Table 3. Kinetics calculations: reaction rate constant and regression coefficients

The Langmuir-Henshilwood kinetics are applied with first-order kinetic similarities as both the absorption process that occurs along with the decomposition reaction take into consideration. Comparison to powder TiO_2/Nd material, TiO_2/Nd material coated with rice husk ash in natural light conditions (-SL) has lower k and R^2 values, however these were found better than that of

TiO_2/Nd/H under dark and UV irradiation. For conditions where the use of UV irradiation the value k is lower than that of natural light may be due to the low intensity of UV radiation and the material has been activated to reduce the forbidden zone energy of material then it can effectively catalyst in the visible area of natural light. In the study of Vaucher et al. (2010), the kinetics of telithromycin photodegradation and oxidative degradation were determined and reported that both photodegradation and oxidative degradation follow first-order reaction kinetics (Vaucher, Paim et al. 2010).

Pseudo-first order kinetic model was commonly used in number of studies to investigate the antibiotic degradation process under the diferent conditions (Zhigang, Wang et al. 2018, Cizmic, Ljubas et al. 2019, Bobirică, Bobirică et al. 2020), photocatalytic degradation of sulfamethazine in aqueous solution using ZnO was reported. The findings showed that 78 and 95% of sulfamethazine were degraded after 60 min irradiation, the rate constant k obtained 2.58×10^{-2} and 4.95×10^{-2} min^{-1} without and with ZnO, respectively.

Figure 9. Concentration of rifampicin remaining versus time according to: zero-order reaction (a), first-order reaction (b) and second-order reaction (c)

The Langmuir-Henshilwood model was studied by Kais et el (2019) and Safari et al. (2015) for photocatalytic degradation of rifampicin and tetracycline, respectively (Safari, Hoseini et al. 2015, Kais, Mezenner et al. 2019). In which, the influence of some parameters and kinetic model were investigated. The results showed that the apparent rate constant (k_{app}) and initial rate constant (r_0) decreased when the initial concentration of rifampicin increased. In sone other studies, the amount of photocatalyst (TiO_2) and pH were considered as significant factors affecting the antibiotic degradation process (Radosavljevic, Golubovic et al. 2017, Kais, Mezenner et al. 2019).

Conclusions

Nano TiO_2 materials in the form of anatase are modified with different Nd content by the sol-gel hydrothermic method using a $TiCl_4$ solution at a temperature of 600°C. The mateiral properties, photocatalytic reactions of the nano TiO_2/Nd and TiO_2/Nd/rice husk ash materials were investigated using modern characteristic techniques. The results showed that Nd doping affects electronic transiti (c) ergy by changing the width of the forbidden zone. Most notably, the modification enha he visible light phototholytic activity of modified TiO_2 compared to pure TiO_2, and depends on the Nd content. The rifampicin decomposition efficiency of nano Nd-TiO_2 material with 0.36% Nd under natural light reaches about 86% after 90 minutes. The TiO_2/Nd/rice

husk ash material are successfully prepared when TiO_2/Nd is coated on rice husk ash by the sol-gel hydrothermical method, with the content of Ti in the material about 0.19% (w/w). Although its photocatalytic reaction efficiency to decompose rifampicin is lower than that of nano Nd-TiO_2 materials (more than 75% after 90 min), this material is suggested to use because after the photocatalytic process, the Nd-TiO_2 material still remains on the rice husk ash carrier. Therefore, Nd-TiO_2 materials will not release in to solution and not cause secondary environmental pollutants. The Nd-TiO_2/rice husk ash material can be recovered in a simple method and able to be long use.

The kinetics of rifampicin removal follows the zero and first-order reaction kinetics especially for TiO_2/Nd-P and TiO_2/Nd/H-SL. The k and R^2 values of TiO_2/Nd/H-D and TiO_2/Nd/H-UV seem to be similar and remarkable lower than that of powder TiO_2/Nd and TiO_2/Nd/H in solar irradiation.

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Figures

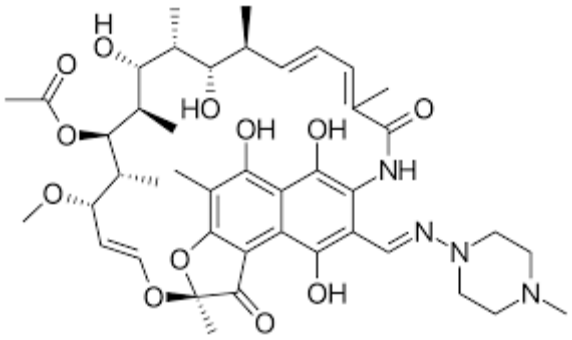


Figure 1. The chemical structure of Rifampicin

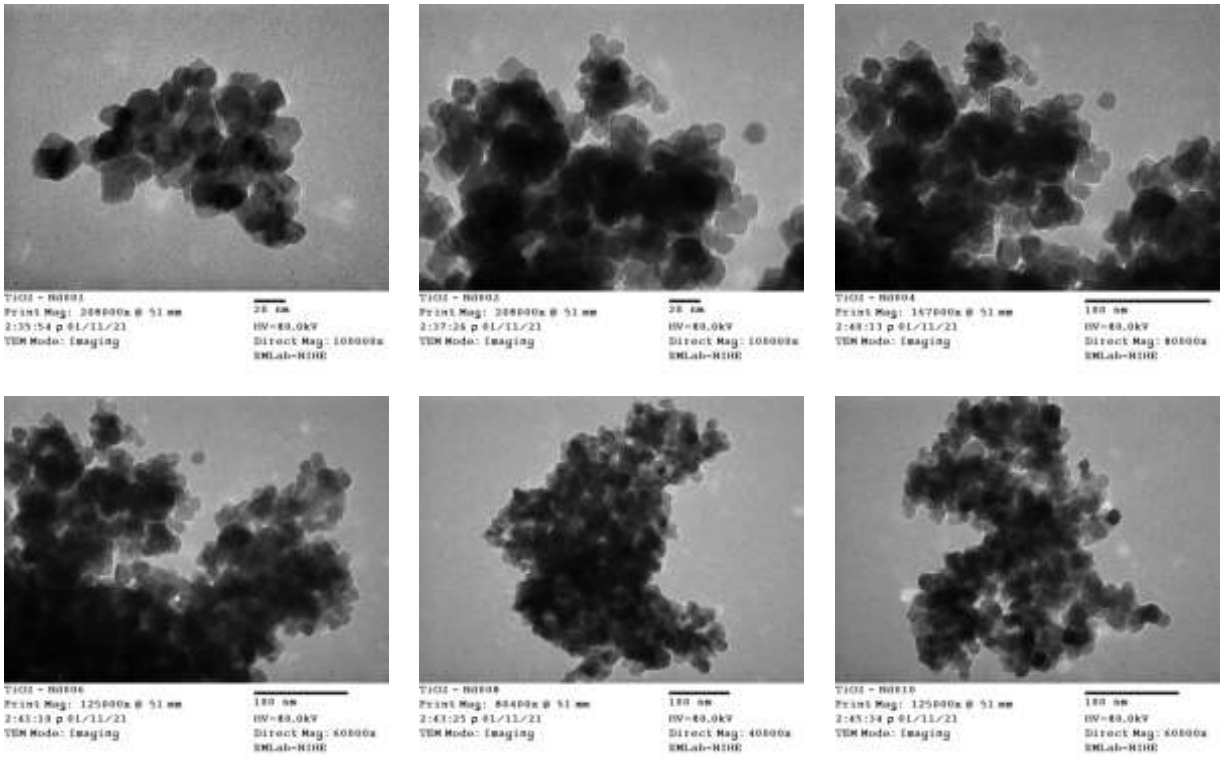


Figure 2. TEM image of TiO_2/Nd modified nanomaterials with different Nd content

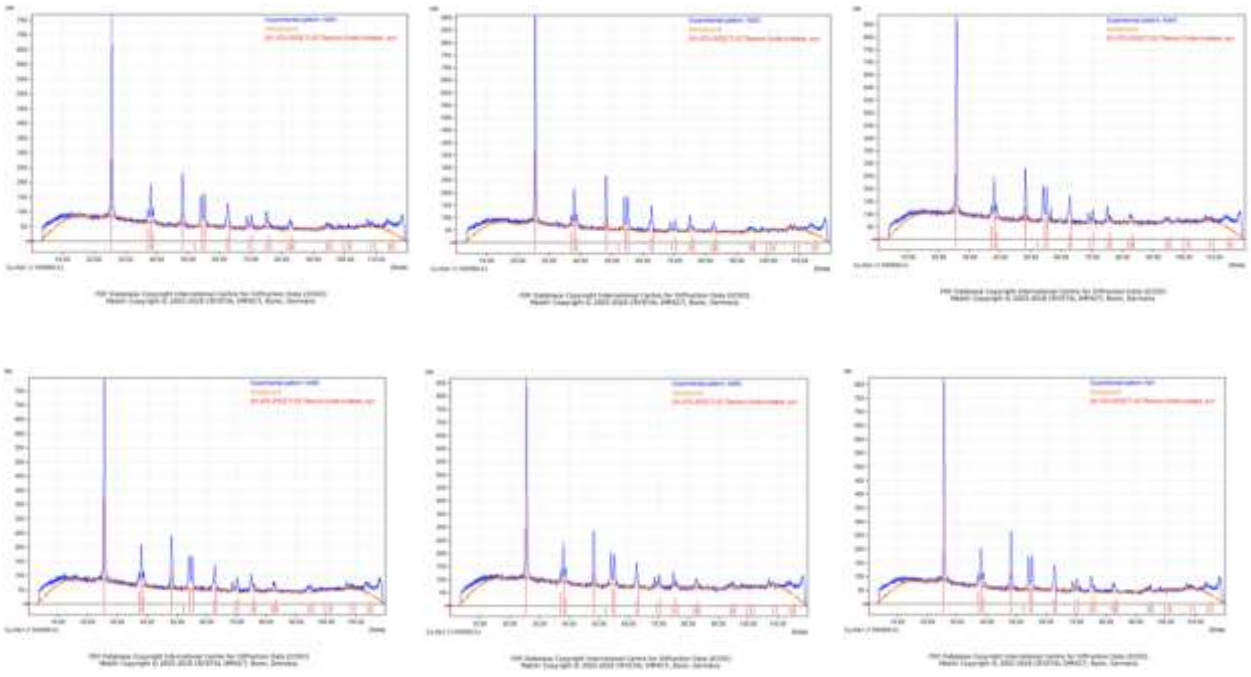


Figure 3. XRD images of nano TiO_2/Nd modified materials with different Nd content

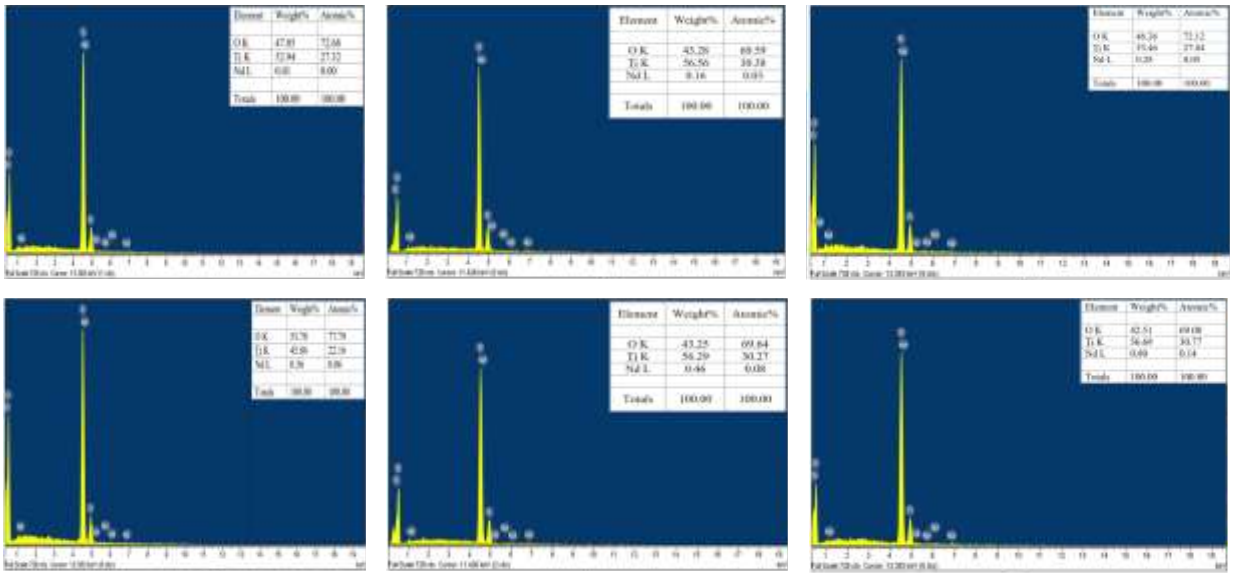


Figure 4. EDX images of TiO_2/Nd modified nanomaterials with different Nd contents

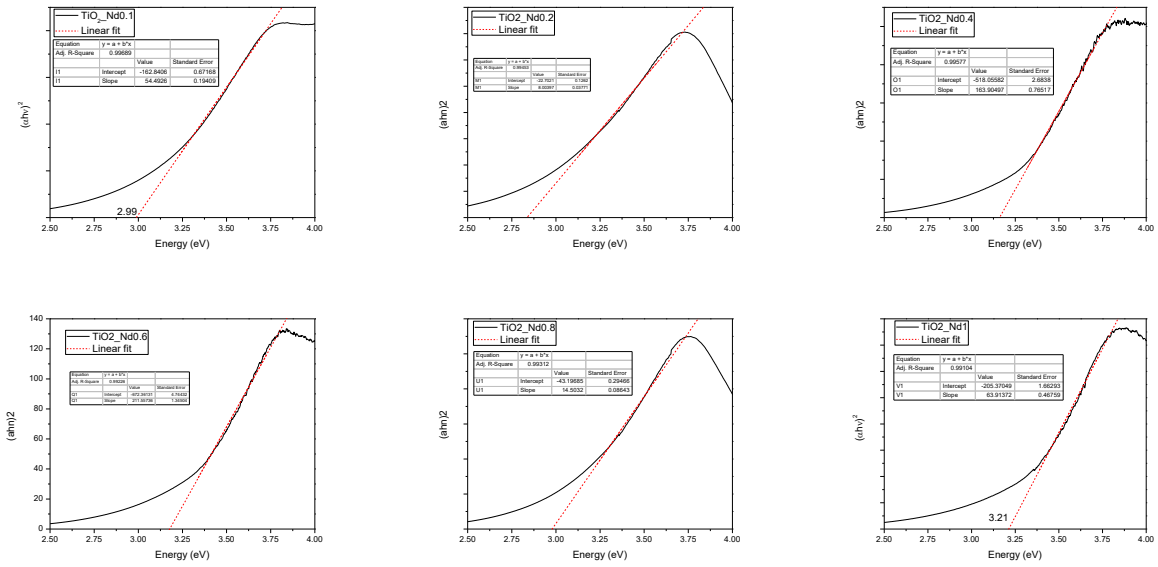
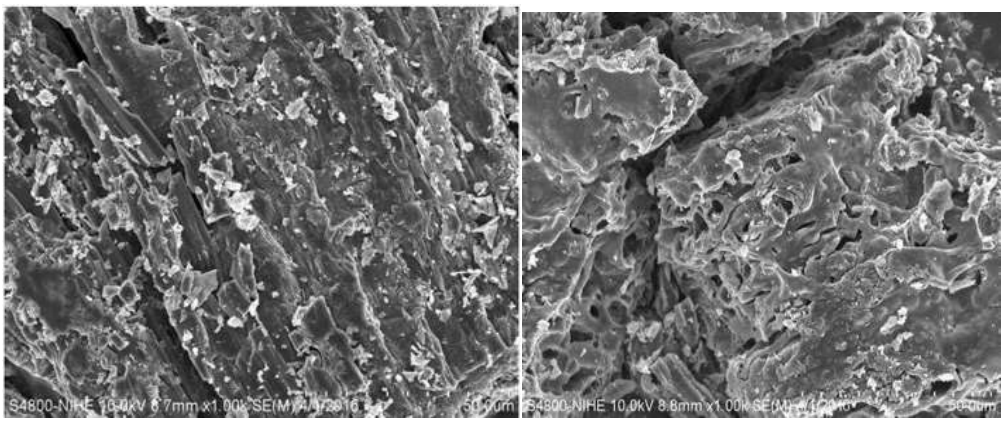
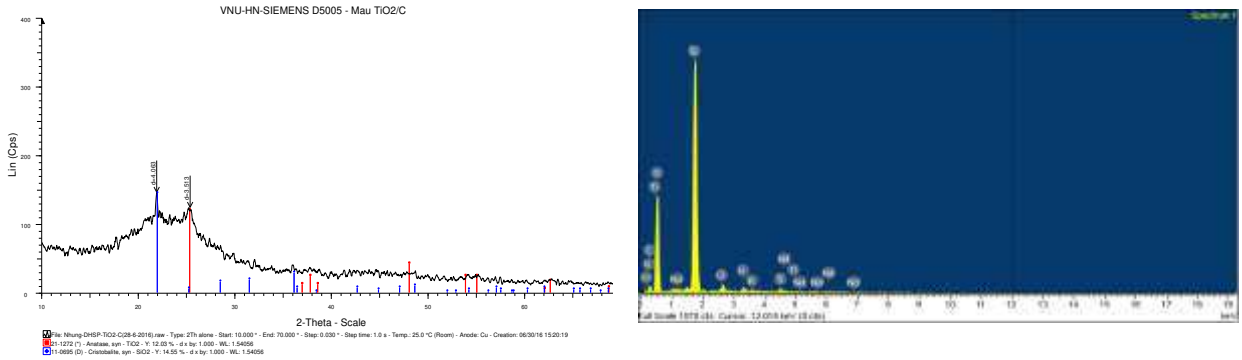


Figure 5. Eg spectrum of TiO_2/Nd modified nanomaterials with different Nd contents



(a) (b)

Figure 6. SEM images of rice husk ash (a) and nano TiO_2/Nd /rice husk ash (b)



(a) (b)

Figure 7. XRD (a) and EDX (b) spectrum of nano TiO_2/Nd /rice husk ash

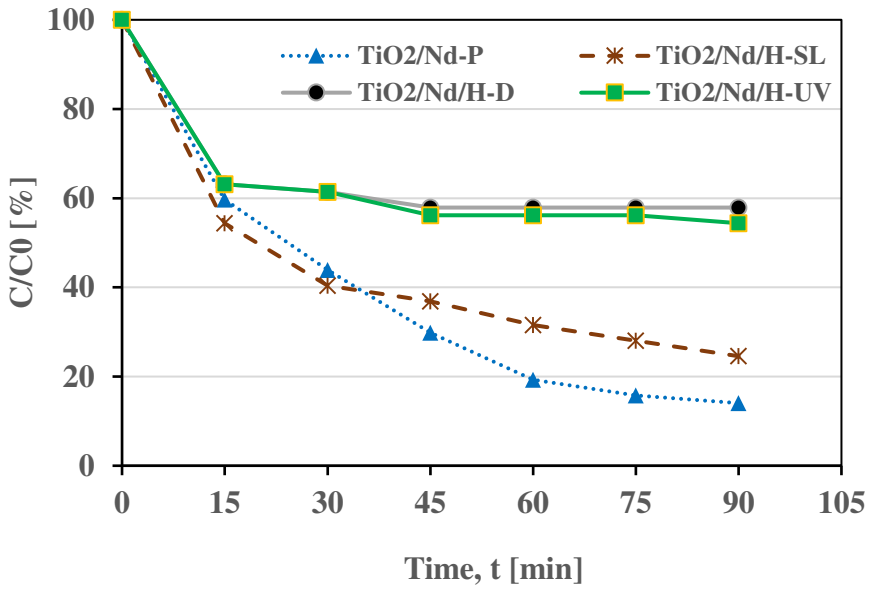


Figure 8. Rifampicin removal efficiency of nano TiO_2/Nd and TiO_2/Nd /rice husk ash under different conditions (TiO_2/Nd-P: nano TiO2/Nd, natural light; TiO_2/Nd/H-SL: TiO_2/Nd/rice husk ash, natural light; TiO_2/Nd/H-D: TiO_2/Nd /rice husk ash, dark)

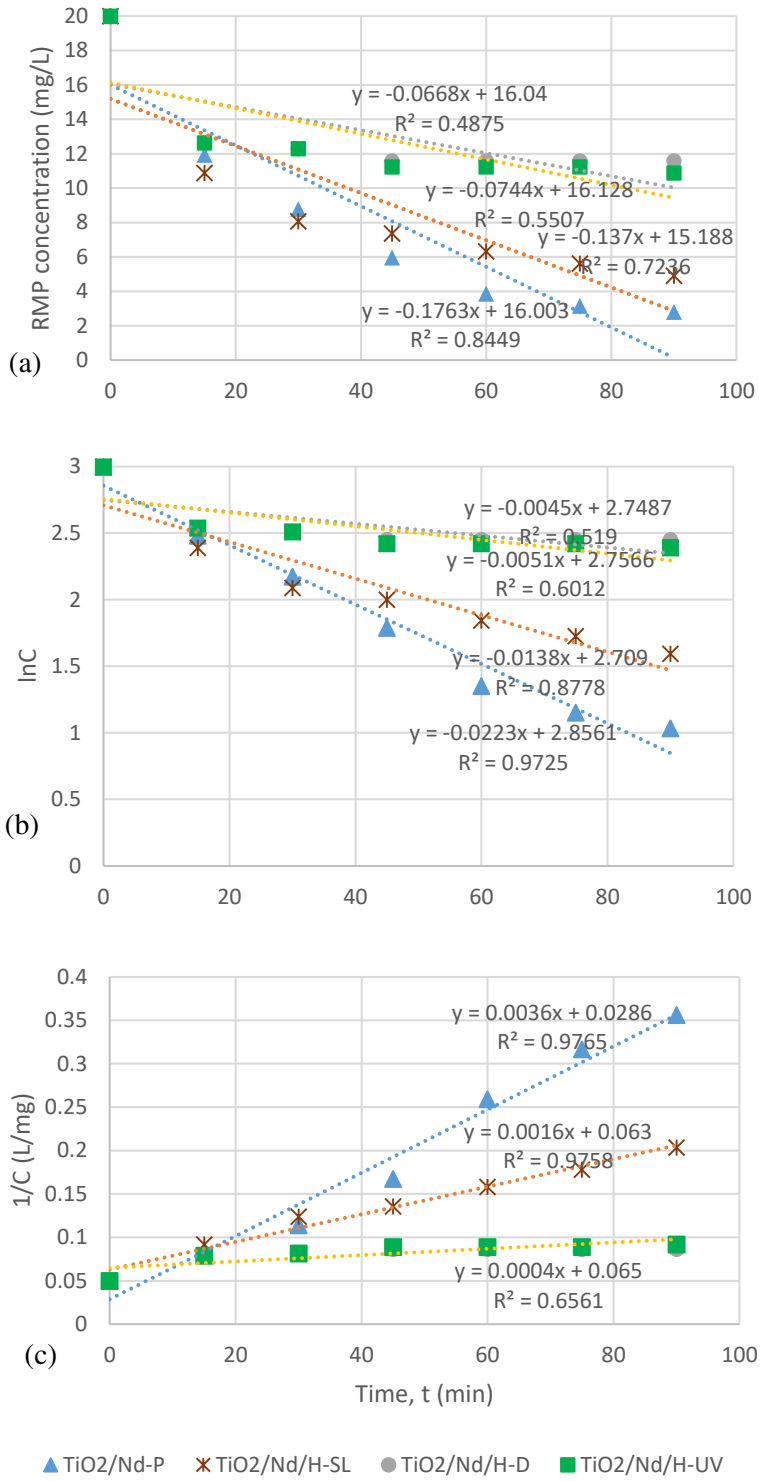


Figure 9. Concentration of rifampicin remaining versus time according to :zero-order reaction (a), first-order reaction (b) and second-order reaction (c)

Tables

Table 1. Composition and rate of chemicals prepared nano TiO_2 modified Nd by the sol-gel hydrothermal method

Chemical	NH_4NO_3 (1.0M)	$(NH_2)_2CO$ (1.0M)	PVA (1.0M)	$TiCl_4$ (0.5M)	Nd^{3+} (1.0g/L)
Volume (ml)	60	450	180	60	0.1-1.0

Table 2. Lattice parameters, particle size and density of *TiO_2/Nd* modified nanomaterials with different Nd content

Nd/TiO_2 ratio (% w/w)	Samples	Lattice parameters		Density, D (g/cm^3)
		a = b (Å)	c (Å)	
0.01	TiO_2- Nd 01	3.770	9.420	3.962
0.16	TiO_2- Nd 02			
0.28	TiO_2- Nd 04			
0.36	TiO_2- Nd 06			
0.46	TiO_2- Nd 08			
0.80	TiO_2- Nd 1			

Table 3. Kinetics calculations: reaction rate constant and regression coefficients

Materials	Zero order kinetic		1st order kinetic		2nd order kinetic	
	k	R^2	k	R^2	k	R^2
TiO_2/Nd-P	0.1763	0.85	0.0223	0.97	0.0036	0.98
TiO_2/Nd-SL	0.137	0.72	0.0138	0.88	0.0016	0.98
TiO_2/Nd/H-D	0.0668	0.49	0.0045	0.52	0.0004	0.66
TiO_2/Nd/H-UV	0.0744	0.55	0.0051	0.60	0.0004	0.66