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ORIGINAL RESEARCH PAPER

Decomposition of petroleum contaminants (naphthol) by ultraviolet (UV) radiation using a green-synthetized titanium dioxide (TiO_2) catalyst

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ABSTRACT

A simple and eco-friendly method for synthesis nanoparticles is using a green chemistry technique. Also, the utilization of green nanoparticles for the treatment of industrial wastewater could be an outstanding plan to confront environmental pollutions. The novelty of this study was to use leaf extract of Stevia Rebaudiana Bertoni for green synthesized TiO_2 NPs and assessing its functioning for the photocatalytic treatment of Naphthol from real sample wastewater in a self-designed photoreactor. The amount of nano-adsorbent changes was studied under different conditions such as the amount of naphthol concentration, pH, and time of degradation. The results of the XRD showed that the Anatase and Rutile phase of TiO_2 conformed to cards no.JCPDS21-1272 and no.JCPDS21-1276 respectively. The EDX analysis illustrated the existence of TiO_2 with a weight percentage of 50.17 wt.% for Ti and 49/83 for O. The size of the particles in the SEM photo was found to be about 17nm. The removal of naphthol content was measured by the UV-Vis method. The optimum pH for naphthol removal by TiO_2 is pH = 9, the optimal contact time is 20 min, and the optimal concentration of Naphthol is 3 mg/L. Comparing the Freundlich and Langmuir adsorption isotherm models revealed that the absorption model in this study is in complete conformity with the Freundlich adsorption model. This study affirms that the green synthesis of Stevia leaf extracted is a modern beneficial procedure for the preparation of TiO_2 nanoparticles. This method is straightforward, cost-effective, eco-friendly, and rapid.

Keywords: *Photocatalytic degradation; Organic contaminants; Green synthesis; Nano-titanium dioxide (TiO_2)*

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INTRODUCTION

The enhancement in human society has expanded the requirement for natural resources. The development of industries has led to the arrival of numerous toxins into the water, soil, and climate that affect all parts of human lives. Water contamination has influenced human wellbeing, oceans, lakes, streams, and biodiversity. A standout among the most critical difficulties for individuals and sciences in ongoing decades is to develop effective techniques to control organic contaminations [1-3].

Nanotechnology has proven to be a viable answer for water and wastewater treatment [4]. Furthermore, it is an eco-accommodating method that helps in converting harmful substances to harmless materials for the environment [4] [5]. Utilizing photocatalyst is one of the best procedures in nanotechnology. Photocatalysts are material that causes the rapid degradation

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of pollutants through the ultraviolet light. At the same time, they are not consumed in the reaction [6-8]. Photocatalysis disintegrates organic pollutants such as synthetic dyes, phenols, pesticides, fertilizers, herbicides, and surfactants [9] [10]. Titanium dioxide (TiO2) nanoparticles are critical and promising photocatalysts that can have high activity in the photodegradation of a wide scope of organic and inorganic contaminants in water and are notable photocatalysts for water treatment. TiO_2 is non-toxic, exceptionally productive, biocompatible, and truly stable under UV [11] [12]. There is a wide range of strategies for synthesizing nanoparticles [13] For example; chemical vapor deposition (CVD), chemical vapor condensation (CVC), mechanical attrition, chemical precipitation, sol-gel techniques, and electrodeposition. These strategies are expensive and are possibly unsafe. In this regard, the green synthesized process is an eco-accommodating method because of using concentrates of plants (leave, blossom, seed, and strips). This technique is very safe, prepared effectively, and versatile for producing at large scales. This technique does not require high temperatures, high energy, and expensive gear and does not involve the dangers of synthetic concoctions [14-17]. The literature on synthesis of TiO2 NPs using various plant extracts like *Syzygium Cumini* [18], *Ocimum Basilicum* [19] , *Trigonella Foenum-graecum* [20], Orange peel [21] and Cinnamon powder [22] is tabulated in Table 1.

Many studies have been done on the removal of organic pollutants in particular synthetic dyes [23-28]. Several studies have proven the capacity of TiO_2 as a photocatalyst to degradation of Naphthol. The function of the process has been studied by many methods such as the impact of the physicochemical parameters on the elimination rates [1], photoactivity of (TiO_2-SiO_2) as a catalyst prepared by a sol-gel method [29], photodegradation dynamic of Naphthol in aqueous TiO_2 [30], and the TiO_2 synthesized by hydrolysis of TiCL [31] $_4$. Hence, in this paper, we report

Table 1. Nanoparticle synthesized from different plant extract

Extract	SEM size (nm)	Reference
Syzygium cumini	18 nm	[18]
Ocimum basilicum	20 nm	[19]
Trigonella foenum-graecum	20 nm	[20]
orange peel	20 nm	[21]
Cinnamon Powder	70 nm	[22]

the green synthesis of TiO_2 nanoparticles using leaf extract of Stevia Rebaudiana and using it as a catalyst for photodegradation of Naphthol under UV. The effects of different parameters on the reaction rate, such as catalyst concentrations, initial pH of the solution, and time duration were studied to determine the optimum treatment conditions. The tests were performed in a self-designed photoreactor for treatment. The effectiveness of green-synthesized TiO_2 was compared with that of two different types of chemical TiO_2. Overall, in this study, it was attempted to invent a simple process of eco-friendly and cost-effective treatment. The results also include the real sample of wastewater.

MATERIALS AND METHODS

Synthesis of TiO_2

In this study, the leaves of *Stevia rebaudiana* are utilized for the union of TiO_2 nanoparticles. *Stevia rebaudiana Bertoni* is an herb, local to South America, which is used as a sweetener and for medical purposes [32]. The samples of the Stevia Rebaudiana Bertoni were prepared in the spring of 2017 from the company Food industry group 111 in the Babolsar- Iran.

The collected leaves (Fig. 1) were washed to clear their dust. They were dried at room temperature for 15 days in a place without any dust. Dried leaves were shrunk into small pieces and sifted to get powder. First, 1 gr of the powder was blended with 50 mL of ethanol, and then it was exposed for 5h to reflux conditions at 50°C. The ethanolic leaf separate was acquired by sifting the blend through Whatman No. 1 channel paper and directly used in the combination of TiO2 nanoparticles.

For the synthesis of TiO_2 nanoparticles, the Erlenmeyer flagon containing 2 mL of tetraisopropoxide ($Ti\{OCH(CH_3)_2\}_4$) in 2 mL of leaf separate was tested while stirring at 50°C. Following 2 h of ceaseless mixing, the shaped TiO_2 nanoparticles dried in the oven at 80°C for 2 h.

Isolated TiO_2 nanoparticles were calcinated at 500°C in a muffle furnace for about 30 min. The calcinated TiO_2 nanopowder was used for further logical methods [33].

Nanoparticle characterization is used for investigating many of its parameters and is the first step after synthesis. It is important for ensuring the physical and chemical properties of NPs. The X-Ray diffraction (XRD) presents data about the crystalline structure and grain size, the disposition of the phases, and compositions. The SEM analysis is used for the high-resolution imaging to the determination of size, dispersion, and morphology of the Synthesized TiO_2. Energy dispersive X-ray (EDX) is a method used for acquiring the elemental compound of a sample [34].

Design of a Pilot Plant for Treatment of Wastewater

To design a pilot plant for the treatment of wastewater and control the contamination of naphthol on surfaces having a photocatalytic cover, an open-top main container was built by Plexiglas sheets having dimensions of 15 cm × 10 cm × 50 cm. Six quartz glass pipes with an internal diameter of 30 mm were placed in three parallel rows, each having two consecutive pipes. Water was entered from one end of the container and was sucked from the other end. The capacity of the pilot is 6 liters.

Through two transparent plastic pipes, water is pumped by two 12-volt car windscreen washing pumps located under the main container. From another container connected to the entrance of the main container, freshwater is sucked in.

A stream of water passes through the container and around the pipes with constant speed. Another mobile container is located above the main container to hold the UV lamps, produced by the Narva Co, LT 15W/009. The process is shown in Fig. 2.

Covering Quartz Glass Pipes with TiO_2 Nanoparticles

Floating coating method: In this method, the coating is done by pushing the quartz glass pipes into the nanoparticle solution (a), waiting for 1 min (b), and pulling them out at a moderate speed (c).

Fig. 1. STEVIA REBAUDIANA BERTONI Plant

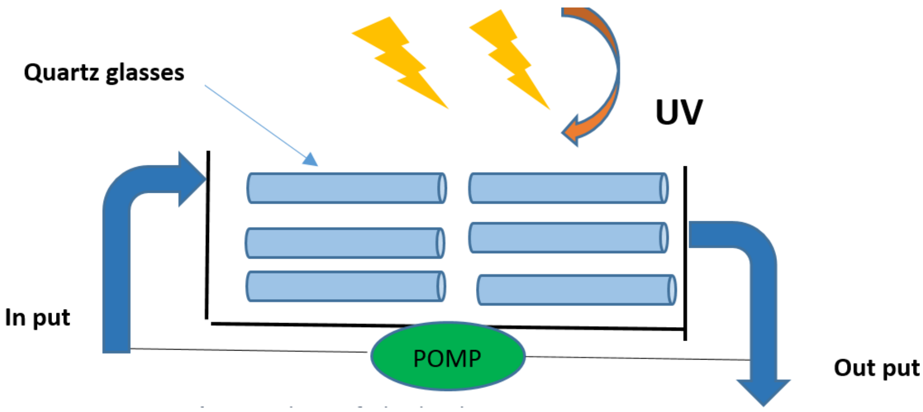

Fig. 2. Scheme of pilot design wastewater treatment

The pullout speed of pipes and the viscosity of the solution are important factors in determining the thickness of the layer. The floating coating method is efficient and fast but has disadvantages such as the thickness of the layer differs from top to bottom of a glass tube, the bottom being thicker. The method is depicted in Fig. 3

For the nanoparticles to stick on the quartz glass, an adhesive material is needed. Coliform (pineal gum) was used for this purpose because it is a natural substance. To coat the quartz glass pipes, they were kept floating for 1 min in the solution containing nanoparticles TiO2 [35]. Afterward, it was withdrawn from the solution by a pence and left in ambient temperature for 1 h to dry up. The process was performed in triplicated to increase the thickness of the layer. As the nano-sites are occupied by the pollutant, the coating was repeated in each stage of adsorption.

Photocatalytic experiments

The quantity of naphthol in the test samples was measured by spectrophotometer according to the procedure described in Section D5530 of the book "Standard Methods of Testing Water & Wastewater by Color Measurement" of 1-Naphthol produced by the Merck. To measure Naphthol, UV-Vis advice was used to assess light absorption by naphthol. The device was set to wavelengths between 200nm and 500nm. Consequently,321nm was measured as the absorption wavelength for measuring the concentration of the Naphthol. The exact concentration was then calculated using the calibration curve that was determined using sets of standard samples with known concentration. The UV-Vis was carried out using the model 300 Varian.

To prepare the stock solution, 0.1 g of naphthol was dissolved in 50 mL of ethanol and was left on a stirrer for 10 min. Then, the naphthol solution was poured in the pilot where UV/TiO_2 photocatalysis pipes are placed.

Therefore, the effects of variable parameters such as pH (5, 7, 9, and 11), contact time (5, 10, 20, 30, 40, 50, 60, and 120 min), and the amount of naphthol (1000, 2000, 3000, and 4000 mg/L) were studied by UV/TiO_2 covered of pipe.

The results were expressed as the removal efficiency (R%) of the adsorbent on naphthol, which is defined as

$$\%R = [(C_\circ - C_1) / C_\circ] \times 100 \qquad (1)$$

where C_o and C_1 are the initial and equilibrium concentration of naphthol solution, respectively.

Adsorption isotherm model

To study the adsorption mechanisms and compare the adsorption rate of Naphthol, we used the Freundlich adsorption model. This model is the basis for studying the energetic surface heterogeneity. Moreover, the Langmuir adsorption model was considered in this regard [36].

The Freundlich (Equation 2) and Langmuir (Equation 3):

$$Log\, q_e = log\, k_f + \frac{1}{n} log\, C_e \qquad (2)$$

where K_f is adsorption capacity (L/mg) and $1/n$ is adsorption intensity [37].

$$\frac{C_e}{q_e} = \frac{1}{q_m K_e} + \frac{C_e}{q_m} \qquad (3)$$

where C_e is the concentration of adsorbate at equilibrium(mg g−1) [37].

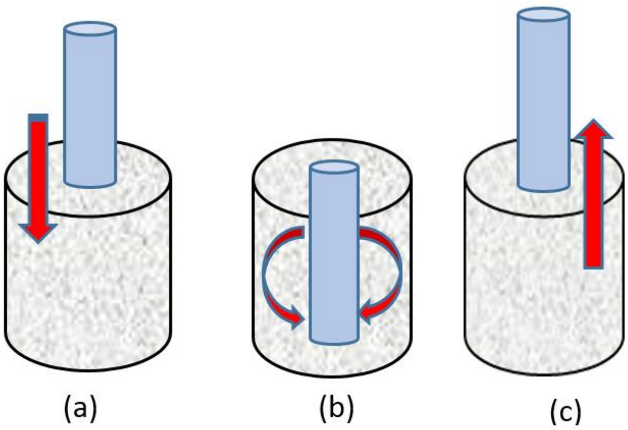

Fig. 3. Scheme of Floating coating method for covering glasses by TiO_2

RESULTS

Results of XRD Analysis

TiO_2 has three phases of Anatase, Rutile, and Brookite. Fig. 4 depicts the XRD pattern of the Anatase and Rutile phases in the synthesized sample.

The anatase phase of TiO_2 conformed to card no.JCPDS21-1272 peaks at 2θ values of 25.2°, 37.9°, 48.1°, 53.9°, 55.1°, 62.9°, 70.2°, and 75.1° and the Rutile phase conformed to card no JCPDS-21-1276 peaks at 2θ values of 27.1°, 36.1°, 41.1°, 54°, and 55.3°. Comparing the peak of the synthesized sample to a reference sample with the reference sample reveals that all the peaks conform to the reference sample of TiO_2. It can be said that the Anatase phase is thermodynamically semi-stable and is also useful for photocatalyst purposes. Moreover, the Rutile phase is the most stable phase of TiO_2. The XRD device model was ARL PERFOMIR.

Results of EDX Analysis

The EDX spectrum is simply a graph that is drawn based on X-ray received from each energy level. Each peak of the graph is related to one atom and therefore indicates one element.

The EDX spectrum Fig. 5 shows that the presence of energy peaks at Okα, TiKα, and TiKβ, suggesting the existence of Ti and O elements in the synthesized nanocomposite. The weight percent of each element is shown in Table 1. The weight percent of Ti and O was 50.17 and 49.83,

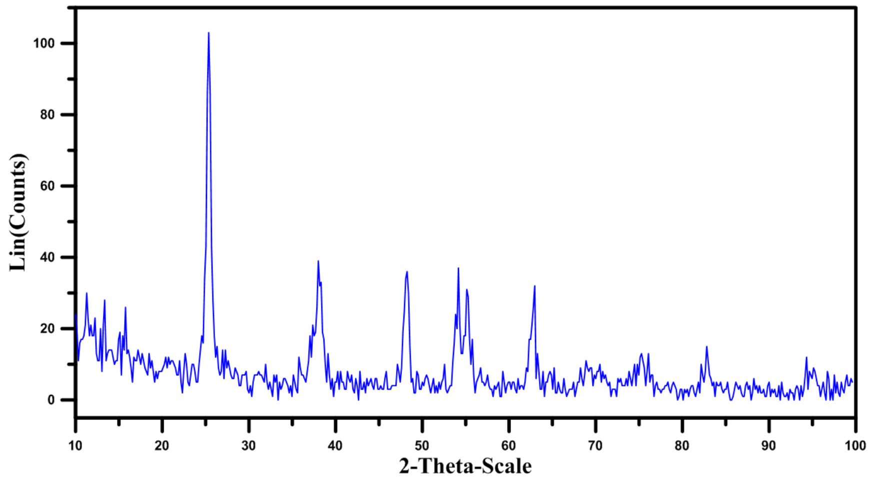

Fig. 4. The XRD pattern of TiO_2

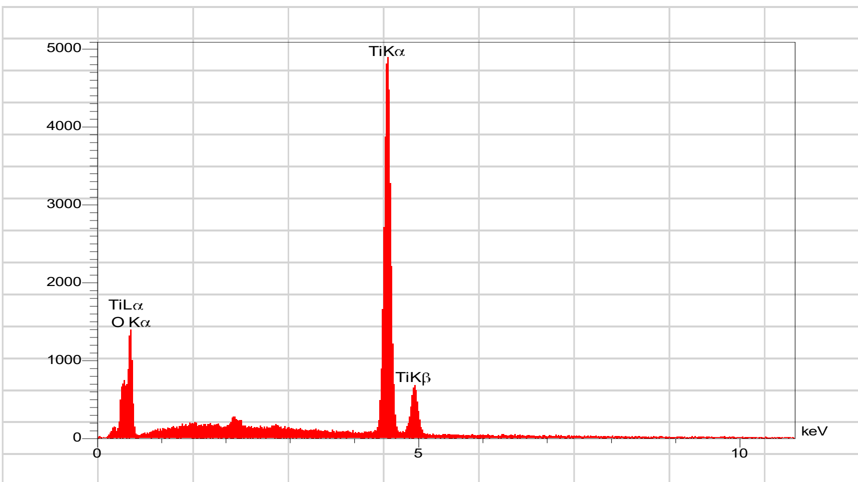

Fig. 5. The EDX pattern of TiO_2

respectively, which is exactly equal to the ratio of nanocomposite in the determined condition.

Results of SEM Analysis

Photos captured from the surface of the synthesized material by SEM model VEGA/TESCAN-XMU at enlargements of 200 nm and 100 nm are shown in Fig. 6. As can be seen, at 200 nm enlargement, grains were synthesized as particles close to each other with a uniform structure with dimensions of about 23 nm. Few empty spaces exist between the grains, which can are denoted by dark colors. Also, the photos at 100 nm enlargement show smaller particles with a diameter of about 12.45 nm. Findings of microscopic studies on the morphology of TiO_2 show that the grain and semi-amorphous structure.

The average dimension of the particles in the SEM photo was found to be about 17 nm, which is consistent with the dimension of the particles calculated by the Scherrer equation and the XRD analysis.

$$D = \frac{k\lambda}{\beta.cos\theta} \quad (4)$$

Where D represents the average grain size of the material. K- is Debye Scherrer Constant (= 0.94), λ is the wavelength of the radiation, and β is the full-

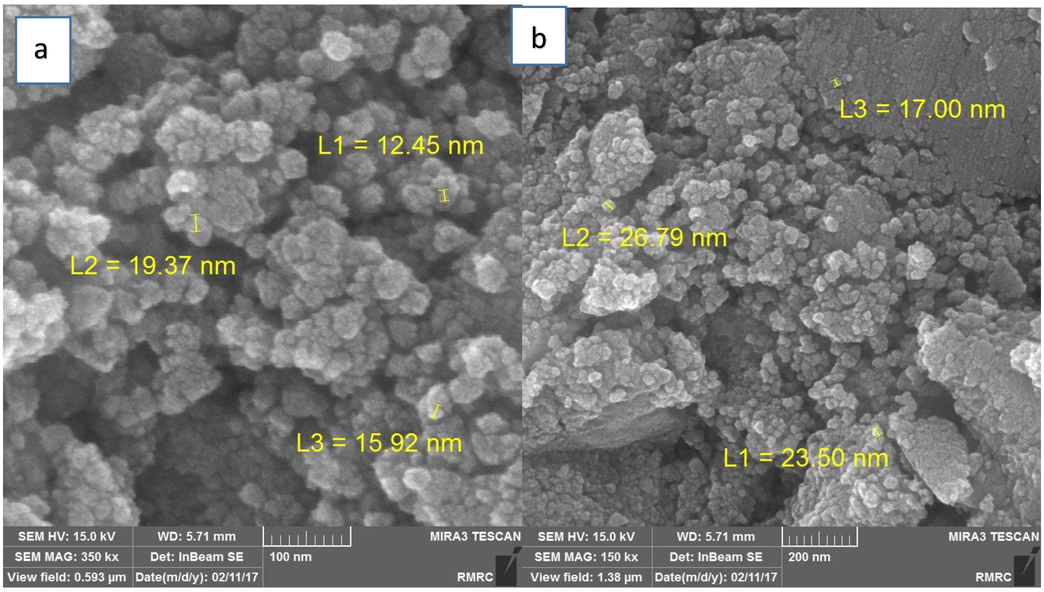

Fig. 6. SEM Imaging of TiO_2 (a)100nm and (b)200nm

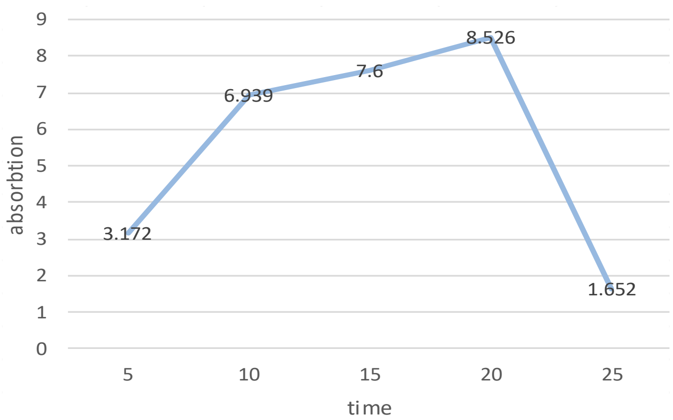

Fig. 7. The effect of time on adsorbtion of naphthol by TiO_2

width half maximum of the peak, θ is the Braggs angle.

Optimization of time

To obtain the optimum contact time duration, the effect of time variation on naphthol adsorption by TiO_2 was investigated for durations of 0, 5, 10, 15, 20, and 25 min. The test was performed in triplicate. The results are listed in Fig. 6. The data of results of the tests on the variation of contact duration of TiO_2 exclusion of naphthol indicate that the maximum and minimum amount of exclusion occurs after 20 min and 5 min, respectively. Duration of contact is another important parameter in the study of adsorption.

Results indicate that by prolonging the duration of contact, the naphthol adsorption percentage increases so that after 20 min of contact of naphthol with TiO_2, the concentration of naphthol decreased by 8.5%. After 25 min of contact with adsorbent, the percentage of naphthol decreased drastically, probably due to the occupation of active TiO_2 sites. The results are shown in Fig. 7.

Optimization of pH

To determine the effect of acidity on the adsorption of naphthol by TiO_2, the test was performed at the pHs of 5, 7, 9, and 11. These tests were conducted to obtain the optimum pH. Results from the tests are shown in Fig. 8. Based on the obtained results, the maximum and minimum adsorption occurs at pH=9 and pH=5, respectively.

Results of the exclusion of naphthol pollutants by TiO_2 nanoparticles indicate that variation of pH in pure water containing naphthol increases the effect of this parameter on the exclusion of naphthol. As can be seen, by increasing pH from 5 to 9, exclusion increases substantially. The explanation for this result is that at acidic pH, H+ ions compete with naphthol to occupy adsorption sites and lead to a low rate of adsorption. Also, at acidic pH, amino groups are protonated and adsorption is reduced.

At higher pHs, ions are more capable to adsorb, and the exclusion of naphthol increases drastically. According to these results, the optimum pH for the adsorber to exclude naphthol stands is 9.

Optimization of Naphthol concentration

Tests were carried out to determine the effect of the concentration of Naphthol at 1000, 2000, 3000, and 4000 mg/L. These tests were conducted to determine the optimum concentration of Naphthol for eliminating the pollutants. The test results are shown in Fig. 9. Results indicate that the maximum and the minimum elimination of the pollutant occur at the original concentration of 3000, and 1000 mg/L respectively.

To select the most effective dose of naphthol, adsorption tests were made at doses of 1000, 2000, 3000, and 4000 mgr/L of naphthol. Results indicate that the highest exclusion of naphthol in the sample occurred at the concentration of 3000 mg/L. At such a concentration, the exclusion of 86.92% of the original naphthol was observed. By increasing the original dose of naphthol to more than 3000 mgr/L, the adsorption percentage decreased.

Real sample

In this section, the adsorption of Naphthol in the real sample by TiO_2 was studied. The test

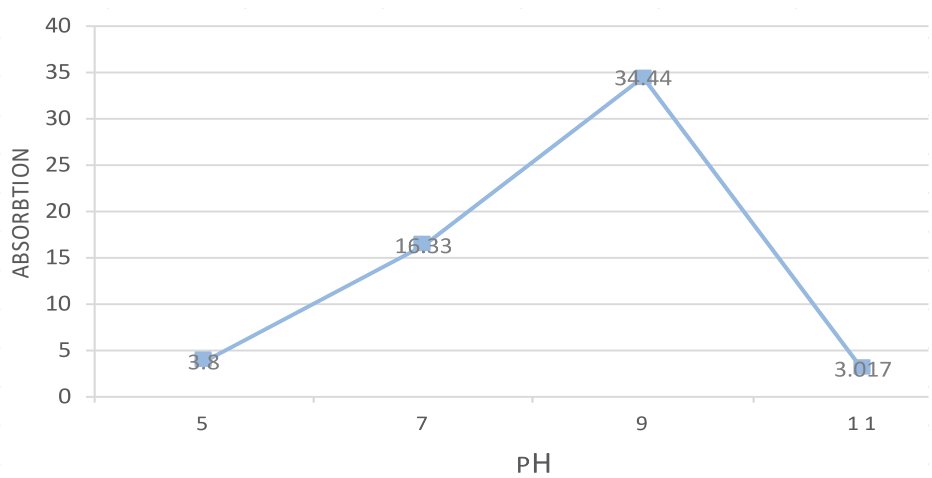

Fig. 8. The effect of pH on adsorbtion of naphthol by TiO_2

was carried out at the optimum acidity (pH = 9) and contact duration (25 min). The results of this test showed that the concentration of Naphthol in contact with TiO_2 and ultraviolet radiation diminished from the original concentration of 0.284 mg/l to a concentration of 0.0062 mg/l. The adsorption was calculated by Eq. (1) to 78.16%. Therefore, it can be concluded that under ultraviolet radiation, TiO_2 can eliminate a high percentage of Naphthol in real wastewater (> 70).

Table 2 shows a comparison between using leaf extract for TiO_2 synthesized to TiO_2 Degussa p 25 [29] and Hydrolysis TiO_2CL_4 [31]in the rate of Naphthol degradation by each one and also time duration of the process in different reactors. It can be seen that the degradation rate by green synthesized TiO_2 is higher and faster than Degussa p 25 and hydrolysis TiO_2CL_4 synthesized by chemical method. The degradation rate for green synthesized TiO_2, Degussa p 25, and hydrolysis TiO_2CL_4 are 86.92%, 80%, and 82%, respectively, and time duration is 20 min, 90 min, and 3 h, respectively.

Results of adsorption isotherm

By comparing the Freundlich and Langmuir adsorption isotherm models, it is concluded that

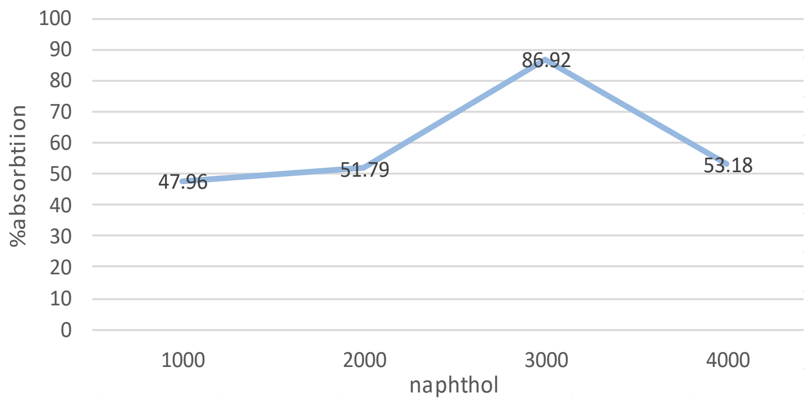

Fig. 9. The effect of Naphthol concentration on asorbtion of Naphyhol by TiO_2

Table 2. Comparison between three types of synthesized TiO_2

Catalyst	Reactor	pH	Time	Degradation of Naphthol
TiO_2 (Degussap25)	Dynamic photoreactor	11	3 h	80%
Hydrolysis TiO_2CL_4 TiO_2 - AC	Microwave thermal	11	90 min	82%
Green synthesis using leaf extract	Self-design photoreator	11	20 min	86.92%

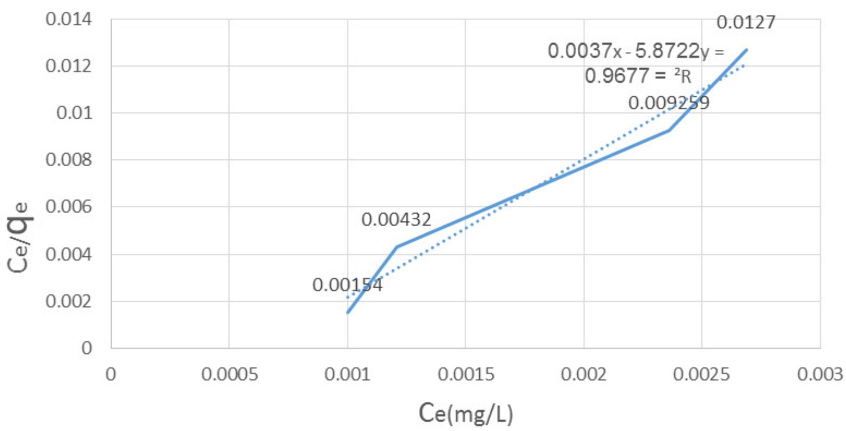

Fig. 10. The langmuir adsorbtion isotherm model

Table 3. The quantitative results of EDX for TiO_2

Elt	Line	Int	K	Kr	W%	A%	ZAF	Pk/Bg
O	Ka	225.5	0.1655	0.0882	49.83	74.84	0.1770	79.57
Ti	Ka	1270.7	0.8345	0.4449	50.17	25.16	0.8868	82.31
			1.0000	0.5331	100.00	100.00		

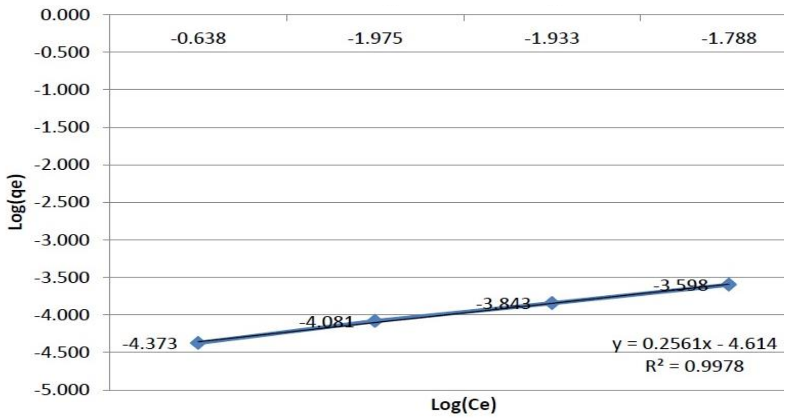

Fig. 11. The Freundlich adsorbtion isotherm model

the adsorption model in this study is in complete conformity with the Freundlich adsorption model. By comparing the R^2 graph (Freundlich R^2=0.9978 and Langmuir R^2=0.9677), it was observed that adsorption is best described by the Freundlich model. The graphs of these models are shown in Fig. 10 and Fig. 11.

Conforming to the Freundlich hypotheses, the adsorption energy of TiO_2 decreases by increasing surface saturation.

CONCLUSION

In this study, the swift and efficient synthesis of resistant TiO_2 nanoparticles using STEVIA leaves extracts solution is presented. The structural and morphological properties of synthesized nanoparticles were characterized. The results of the XRD showed that the Anatase and Rutile phase of TiO_2 conformed to cards no.JCPDS21-1272 and no.JCPDS21-1276 respectively. it showed that the TiO_2 samples are synthesized with higher crystallinity and purity The EDX analysis illustrated the existence of TiO_2 with a weight percentage of 50.17 wt.% for Ti and 49/83 for O. Based on the SEM images, the prepared nanoparticles exhibit morphology and particle size in the range of 12.47nm and 17nm. The substance had a nanostructure with an equal size compared with the green synthesized of Syzygium Cumini [18], Ocimum Basilicum [19], Trigonella Foenum-graecum [20] , Orange peel [21] and Cinnamon powder [22].

The TiO_2 performs better in the adsorption of the pollutant (Naphthol) in an acidic environment. According to the designed pilot and limited contact surface of nanoparticles with the pollutant (Naphthol), the occupied nanoparticles were not capable of further adsorption after 20 min. In this regard, the most effective concentration by which the designed system is capable of adsorption was 3000 ppm Naphthol. The results illustrated that the nanoparticles could eliminate the high concentration of naphthol in a short time. The isothermal model discovered that the Freundlich isotherm explains better the adsorption of the Naphthol to the TiO_2 NPs.

A comparison proves that the degradation rate by green synthesized TiO_2 is higher and faster than Degussa p 25 and hydrolysis TiO_2CL_4 synthesized by chemical method. This study confirms that the green synthesis of Stevia leaf extracted is a modern beneficial procedure for the preparation of TiO2 nanoparticles. This method is straightforward, cost-effective, eco-friendly, and rapid. Thus, it can be utilized as a practical and upstanding way for the removal of contaminants from industrial wastewater and could be a step to sustainable development and management.

CONFLICT OF INTEREST

The authors declare no conflict of interest in this study.

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