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ARTICLE

INVESTIGATING OF REMOVAL ACTIVITY OF SYNTHESIZED ZINC TITANIUM OXIDE NANOPARTICLES ON THE WASTEWATER TREATMENT

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ABSTRACT

In this study, ZnTiO3 nanoparticles were successfully prepared by sol-gel method. For preparation of these nanoparticles, zinc acetate and tetra-n-butyl orthotitanate were used as the sources of zinc and titanium, respectively. Stearic acid was used as the complexing agent. Infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM) were used for characterization, phase detection, and determination of the size and morphology of the particles, respectively. The size of the synthesized zinc titanium oxide nanoparticles was obtained approximately between 37-56 nm.To investigate the efficiency of the synthesized nanoparticles in removal of pollutants, malachite green was used as the model pollutant. To obtain the optimum condition, the effects of concentration, pH, time, and the amount of ZnTiO3 adsorbent were investigated. Studies showed that ZnTiO3 nanoparticles demonstrated good efficiency in removal of malachite green.

KEY WORDS
Nanoparticle, removal, ZnTiO3, sol-gel, malachite green

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INTRODUCTION

Healthy water which is free of toxic chemicals and pathogens is necessary for human health and it is considered a crucial material in major industries such as electronics, pharmaceuticals, and food industries. Due to expansion of drought, increase of population, intensification and improvement of health regulations, and increase of water consumption, supplying healthy water for the world is becoming challenging [1].

Though 2/3 of the surface of the earth is covered with water, nowadays there is water scarcity in human societies. With the increase of the world population, increase of drinking water consumption on one hand and contamination of a remarkable portion of drinking water on the other hand, will accelerate the decrease of drinkable water sources. According to the United Nations predictions, 48 countries (i.e. 32% of the world's population) will face water shortage in 2025 [2].

Underground waters finally find their ways into the rivers and seas. Therefore, contamination of underground waters can be a serious bio-environmental hazard. Dye pollutants are relatively much more hazardous compared to other pollutants. In fact, the color of these pollutants is a factor which can be used for detection of dangerous pollutants. Textile waste water is known as one of the biggest sources of pollutants which leave bio-environmentally destructive impacts. The dye material present in these waste waters is potential hazards for underground waters and inhabitants of these ecosystems. Water scientists and engineers are working toward increasing water quality according to the strict regulations and standards as water consumption is increasing. There are different methods to remove this substance from the aqueous solutions including adsorbent materials [3-6]. Beak et al. investigated MG removal from the aqueous solutions by degreasing coffee beans [7]. Rais Ahmad and coworkers studied the adsorption of MG on the Ginger wastes (TGW) by batch and column methods. The effect of various factors were also studied including initial dye concentration, contact time, pH and temperature [8]. The progresses of engineering sciences at the nano scale have provided unprecedented opportunities for development of acceptable processes for cost effective and bio-environmentally compatible water purification. To purify textile waste water and remove dyes from it various methods can be utilized. One of the most cost effective and common methods is application of adsorbents capable of trapping the dyes present in these waste waters. These adsorbents have different types which can be categorized in different groups according to their adsorption capacity, yield, and their efficiency in removal of these dyes [9-12]. Titanium dioxide nanoparticles have relatively wider application in removal of bio-environmental pollutants [9]. Many researchers have taken advantage of using adsorbent for removal of pollutants [13-18]. Novelty of this research is the application of zinc titanium oxide nanoparticles as the adsorbent in removal of pollutants, for the first time. For preparation of these nanoparticles, sol-gel method was used due to simplicity and controllability of the morphology of the nanoparticles.

MATERIALS AND METHODS

The Instruments and material

Scanning electron microscopy (SEM) was used for determination of particle size. FT-IR (Perkin Elmer) and XRD instruments were used for investigation of structural properties of the nanoparticles. A dual-beam spectrophotometer (Perkin Elmer UV/Vis 25) was used for measurement of the sample absorbance. Furthermore, a pH meter (Mettler Toledo) was used for pH measurement. Zinc acetate, tetra-n-butyl

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orthotitanate, and stearic acid were purchased from Merck Company of Germany. Deionized water was used during the experiment for preparation of the solutions.

Zinc titanium oxide nanoparticles preparation method

In this study, a type of wet chemistry synthetic procedure, stearic acid gel was used for preparation of pure zinc titanium oxide nanoparticles. In addition, this synthetic procedure is easily controlled and is an appropriate method. Sol-gel method demonstrates interesting results such as low temperature, homogeneity and higher purity. At first, zinc acetate (1 mol) and tetra-n-butyl orthotitanate (1 mol) were added to 2 moles of melted stearic acid at 73 ˚C and stirred. Then, it was put in an electric oven and heated up to 400 ˚C to dry up. It was kept at the same temperature (400 ˚C) for another 1 h to remove the stearic acid impurities. Finally, the temperature was raised up to 850 ˚C with a rate of 5˚/min to complete the calcination process. The zinc titanium oxide nanoparticles were ready for FT-IR, XRD and SEM analysis.

Procedure

In this research, some zinc titanium oxide adsorbent was added to the solutions of malachite green with different concentrations at ambient temperature. Then, at different time intervals, free concentrations of the solutions were recorded by a dual-beam spectrophotometer. The optimum factors such as pH, contact time, concentration of MG and the amount of adsorbent were determined from diagrams according to the above factors.

RESULTS AND DISCUSSION

Characterization and investigation of zinc titanium oxide nanoparticles

Characterization by infrared spectroscopy

[Fig. 1] illustrates the infrared spectrum of the zinc titanium oxide nanoparticles. In the FT-IR spectrum, the bands at 548.76 cm^{-1} and 836.81 cm^{-1} refer to the formation of $ZnTiO_3$. Furthermore, the absorption band at 3434.06 cm^{-1} in the spectrum, is attributed to the stretching vibrations of –OH groups of water.

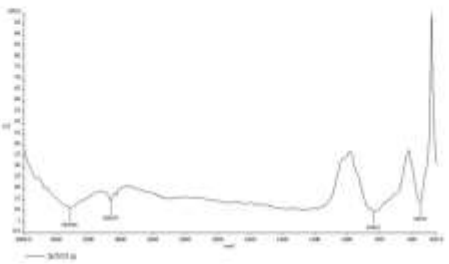

Fig. 1: FT-IR spectrum of zinc titanium oxide nanoparticles.

Investigation of the phase and morphology of zinc titanium oxide nanoparticles by X-ray diffraction method

[Fig. 2] demonstrates the XRD pattern for zinc titanium oxide nanoparticles. According to the results, the formed nanoparticles are of cubic type which is in complete agreement with single XRD data. It should be noted that, there are very little amounts of titanium dioxide in the products which can be easily ignored.

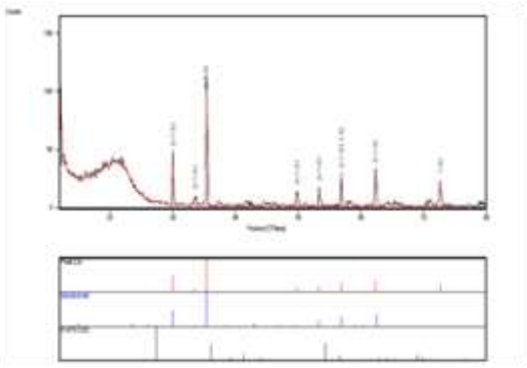

Fig. 2: XRD pattern of zinc titanium oxide nanoparticles.

Investigation of scanning electron microscopy spectrum

[Fig. 3] shows the scanning electron microscopy spectrum of the zinc titanium oxide nanoparticles. As shown in this fig., the average particle size obtained is around 41 nm.

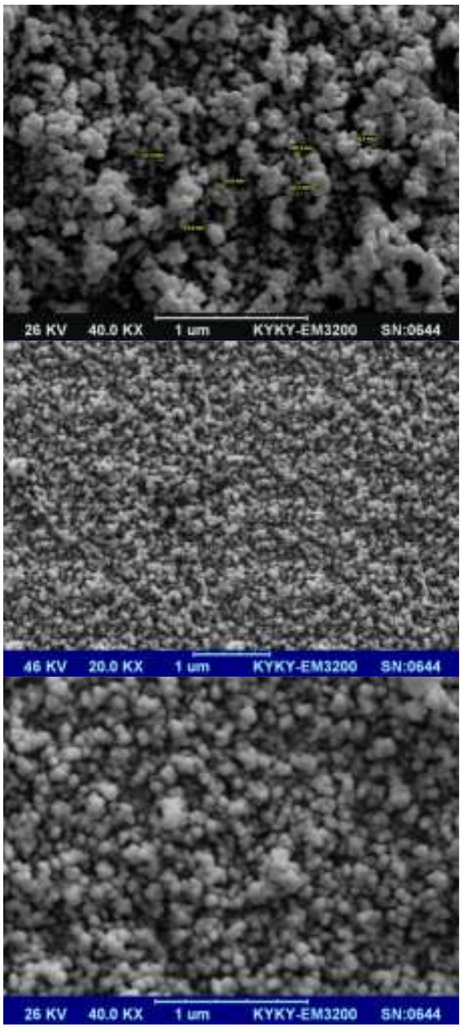

Fig. 3: SEM images of zinc titanium oxide nanoparticles.

Investigation of the efficiency of zinc titanium oxide adsorbent in removal of malachite green pollutant

Plotting the calibration curve for malachite green adsorption versus its different concentrations

For measuring the concentration of MG, its absorption properties in UV-Vis region were used. The absorption spectrum was plotted by a dual-beam spectrophotometer within the range of 350-800 nm for 1-10 ppm samples of malachite green to determine the maximum wavelength. As shown in [Fig. 4], the maximum absorption for malachite green is at 625 nm. Hence, this wavelength was used to measure the concentration of malachite green.

Plotting the calibration curve is essential for determination of the concentrations of the samples whose colors have been removed by absorbent. Thus, different concentrations of the malachite green were prepared and their absorptions were recorded and presented at 625 nm. The calibration curve in [Fig. 5] is plotted on the basis of the data presented in [Table 1].

Table 1: Concentration changes and absorptions

Concentration of malachite green (mg/L)	Absorption
1	0.201
2	0.601
3	0.9754
4	1.4183
5	1.9118

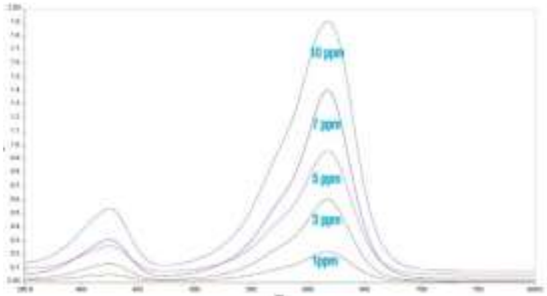

Fig. 4: UV-Vis spectrum of Malachite green.

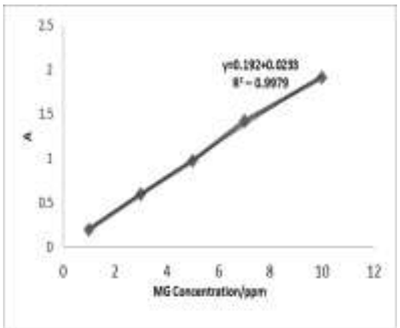

Fig. 5: Calibration curve of malachite green.

Investigation of the removal of malachite green in different pH values

pH is one of the most important factors which can increase the adsorption capacity of the adsorbent considering the point of zero charge potential, pH_{PZC}. To obtain the pH_{PZC}, 1 g of the adsorbent was added to eight beakers and their pH_1 values were adjusted between 2-9 using 0.1 M solutions of NaOH and HCl. Then, their pH_2 values were recorded after 24 h using a pH meter. Finally, ΔpH was plotted against pH_1 and the point where this curve crossed pH_1 diagram was considered as the pH_{PZC} or point of zero charge pH. As demonstrated in Fig. 6 the point of zero charge pH corresponds to the adsorbent 6 in which pH the adsorbent is electrically neutral. Because malachite green is a cationic dye, negative charges must surround the adsorbent. Thus, at pH>6 negative charges surround the adsorbent and the removal rate increases. Table 2 shows pH_1, pH_2, and ΔpH variations according to pH_1, where pH_1 is the hydrogen potential in the first day and pH_2 is the hydrogen potential after 24 h. As shown in table 3, 0.1 g of the zinc titanium oxide nanoparticles was added to 50 mL of 10 mg/L of malachite green and shaken for 30 minutes on a shaker. It was then filtered using a syringe and the absorbance of the solution was red and its concentration was calculated using the calibration curve and then placed in formula (1) to calculate the removal percentage where, C_0 is the initial concentration (mg/L) and C is the final concentration (mg/L) of malachite green and the diagram of removal percentage (R%) is plotted according to pH [Fig. 7]. As observed in [Fig. 7], the maximum amount of removal occurs at pH=8. Therefore, we will use pH=8 for optimization of other parameters.

$$\%Removal = \frac{(C_0 - C)}{C_0} \times 100 \qquad (1)$$

Table 2: pH_1, pH_2, and ΔpH variations according to pH_1

pH 1	pH2
2	-0.8
3	-2.4
4	-3.7
5	-4.9
6	-6
7	-7.2
8	-8.6
9	-10

pH 1	∆pH	
2	1.2	
3	0.6	
4	0.3	
5	0.1	
6	0	PH $_{PZC}$=6
7	-0.2	
8	-0.6	
9	-1	

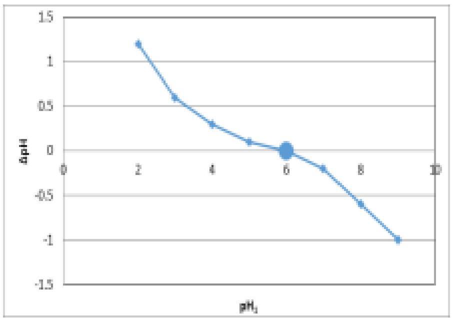

Fig. 6: Diagram of ΔpH variations according to pH$_1$.

Table 3: The effect of pH on the removal percentage

concentration=10 ppm	Volume=50	Time=30	Dosage=0.1
%Removal	A_{30}	A_0	PH
25.38	1.321	1.771	6
51.74	0.727	1.508	7
69.46	0.437	1.432	8
63.92	0.463	1.284	9
		%Removal	PH
		25.38	6
		51.74	7
		69.46	8
		63.92	9

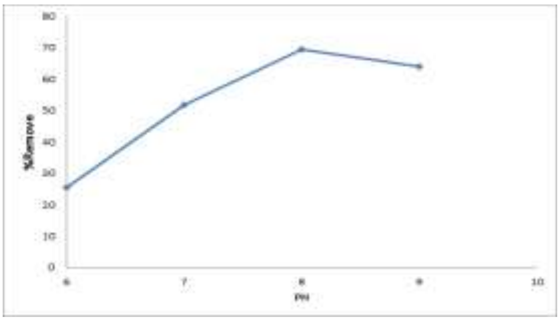

Fig. 7: Diagram of removal percentage of zinc titanium oxide nanoparticles versus pH.

Investigation of removal of malachite green on different dosage of zinc titanium oxide nanoparticles

Different amounts of the zinc titanium oxide nanoparticles were added to 50 mL of 10 mg/L solutions of malachite green with pH adjusted to 8 and were shaken for 30 minutes on a shaker. Then, they were filtered by insulin syringes and the absorbance values of the solutions were recorded. The concentrations were calculated using the calibration curve and placed in the formula (1) to calculate the removal percentage. As [Fig. 8] indicates, the removal percentage increases with the increase of the amount of the adsorbent. This means that following increasing the amount of the adsorbent, the available sites for adsorption and results in improvement of dye removal increase. If the amount of the adsorbent is more than the optimum amount, the condensation and covering the molecular sites of the adsorbent results in a reduction in adsorption rate. According to the [Fig. 8], it is observed that the malachite green removal percentage increases with the increase of the adsorbent dosage until reaching a maximum at a dose of 0.7 g and then remains constant. Thus, the optimum dose of the nanoparticles was chosen as 0.7 g.

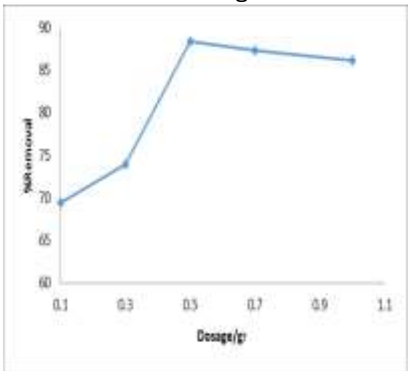

Fig. 8: Removal percentage of malachite green in different dosage of zinc titanium oxide nanoparticles.

Investigation of malachite green removal percentage based on different contact times

0.5 g of the zinc titanium oxide nanoparticles was added to 50 mL of 10 mg/L solution of malachite green with the pH adjusted to 8 and was shaken on a shaker. The absorbance of the solution was measured by a dual-beam spectrophotometer in 20 minutes' intervals after filtration by an insulin syringe. The concentrations were calculated from the calibration curve equation. The removal percentage was calculated by formula (1). [Fig. 9] indicates that the removal percentage reached a constant value after 60 minutes. Therefore, 60 minutes is considered as the optimum contact time for removal of the pollutant malachite green dye from aqueous media.

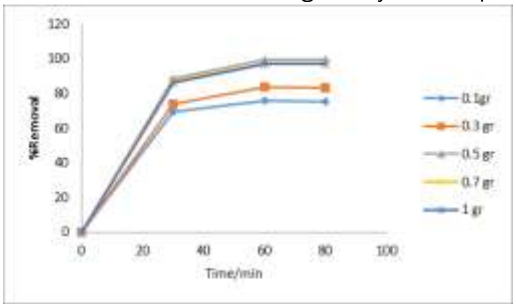

Fig. 9: Removal of malachite green on different contact time.

Investigation of the malachite green removal percentage with different concentration at optimum conditions

Zinc titanium oxide nanoparticles (0.5 g) were added to a 50-mL solution of malachite green with concentrations varying from 1 to 10 mg/L with the pH adjusted to 8. The solutions were shaken for 60 minutes on a shaker and then filtered and the absorbance values were measured by a dual-beam spectrophotometer. The concentrations were calculated using the calibration curve equation and the removal percentages were calculated by formula (1). [Fig. 10] demonstrated that the removal percentage of the solution with lower concentration is higher than the rest.

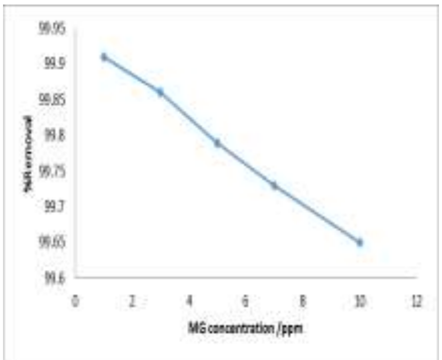

Fig. 10: MG removal percentage using the zinc titanium oxide nanoparticles in different concentrations of MG.

DISCUSSION

Camel was secured in sternal recumbence and fistula was repaired under xylazine sedation. Xylazine @ 0.3 mg/kg body weight administered intramuscularly and local infiltration of 2% Lignocaine was made. Partially masticated feed material was recovered from the buccal fistula along with pocket by help of allies forceps and pocket was emptied. The fistula was debrided. One soft circular leather piece of size slightly greater than diameter of fistula was placed on inner oral mucosal opening along with thread which was come out through buccal fistula opening [Fig. 2]. The wound edge was freshened with B.P. blade to improve vascularity. Buccal fistula was repaired with catgut no. 2 and skin was sutured with silk thread. Another rectangular hard leather piece of size slightly greater than diameter of fistula was placed on outer skin opening of fistula and knot was secured on the outer hard leather piece [Fig. 3].

Table 1: Prediction time of parallel machines and prediction accuracy

Machine	Prediction time	Prediction accuracy
P1	0.29 sec	98%
P2	0.32 sec	98%
P3	0.29 sec	100%
P4	0.31 sec	96%

The wound edge was freshened with B.P. blade to improve vascularity. Buccal fistula was repaired with catgut no. 2 and skin was sutured with silk thread. Another rectangular hard leather piece of size slightly greater than diameter of fistula was placed on outer skin opening of fistula and knot was secured on the outer hard leather piece [Table 1].

CONCLUSION

This research demonstrated that zinc titanium oxide nanoparticles were synthesized successfully by sol-gel method. Infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) were used for characterization, phase detection and determination of the size and morphology of the particles. According to the results, the prepared nanoparticles were of cubic type which was in complete agreement with single crystal XRD data. The size of the synthesized zinc titanium oxide nanoparticles was between 37-56 nm.

Malachite green was used as a model pollutant to investigate the efficiency of the synthesized nanoparticles in removal of pollutants. To obtain the optimum condition the impacts of the concentration of the pollutant, pH, time and the amount of $ZnTiO_3$ were studied. The studies showed that $ZnTiO_3$ nanoparticles demonstrate good efficiency in removal of malachite green.

Hence, according to these results, zinc titanium oxide nanoparticles can be applied as an available adsorbent with high removal percentage.

CONFLICT OF INTEREST
There is no conflict of interest.

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FINANCIAL DISCLOSURE
None

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