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Photocatalytic Activity of Zinc Oxide Nanoparticles Coated on Activated Carbon Made from Mango Seed in Removing Acid Black 1 from Aqueous Solutions

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A-B-S-T-R-A-C-T

Background & Aims of the Study: Discharge of industrial wastewater to the environment has harmful effects. Textile industry is one of the industries that burdens pollutants to the environment. So the wastewater of these industries must be treated before discharging into the environment. Various methods for removing industrial pollutants have been investigated. Among them, AOPs have attracted much attention due to their ease of use, economic efficiency, and high performance. Therefore, the purpose of this study was to investigate the photocatalytic role of ZnO nanoparticles coated on activated carbon made from mango seed as an advanced oxidation process in removal of Acid Black 1 from aqueous solutions.

Materials & Methods: This experimental research was performed in a 1000 cc batch reactor. In this process, effect of initial pH (3-9), initial dose of Acid Black (20-200 mg/L), modified photocatalyst concentration (20-100 mg/L) and reaction time (5-30 min) were investigated. The reactor contained of a 55-watt low-pressure mercury lamp inside a steel chamber.

Results: The results showed that in this reserch the max removal efficiency of Acid Black 1 at pH=3, contact time of 30 min, initial dose of "Acid Black 1" 100 mg/L and modified photocatalyst dose of 0.1 g/L, was equal to 95%.

Conclusion: This process had a high efficiency for Acid Black 1 Removal and it can be used to reduce the dye concentrations in textile wastewater before final discharge to the environment. Due to the lack of sludge and waste production, this environmental friendly process showed a remarkable potential for the purification of industrial effluents.

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Background

Due to the rapid development of industries and the increase of wastewater production from these industries, contamination of the environment with industrial pollutants, especially wastewater, had become a major environmental issue (1,2). Most of industries, such as the cosmetics, leather, printing and textile, produce wastewater containing various dye pollutants. Every year, about 106 tons of dyes are produced with various formulas worldwide (2). Dyes have a complex molecular structure and are often toxic, carcinogenic (production of amine groups in anaerobic decomposition), mutagen, Non-biodegradable and resistance, which could cause destructive effects on the environment (2-4). The textile industry is one of the world's largest dye consumers, with about the 10-20% of the world's total dye usage. When a dye containing wastewater enters the environment, especially in water resources, it disrupts the aesthetic and ecological aspects. Eutrophication and algal bloom in surface waters is one of the most common problems of dyes in the environment. The presence of organic dyes in the wastewater of above mentioned industries, in the case of inadequate treatment, could lead to reduce in the quality of surface and ground water resources (4). Acid Black 1 is an artificial dye that is resistant to various treatment processes and sunlight. Today, due to its cost-effectiveness, the use of this dye has flourished in the textile industry. In addition to color pollution of water by Acid Black 1, the degradation of this dye in the environment produces toxic and mutagenic compounds (5). Various treatment methods such as biological degradation, use of fungi and actinomycets, chemical oxidation/reduction processes, advanced oxidation processes such as O3/UV-O3/H2O2 - O3/UV/H2O2, TiO2/UV and Photophenton, adsorption on activated carbon, bio-absorption, membrane processes and conventional coagulation have been used to remove dyes (6-9). AOPs are based on the production of strong oxidizing radicals such as hydroxyl radical, sulfate radical, superoxide radical and hydroperoxyl radical, which have a high tendency to degrade pollutants (10,11).

In photocatalytic degradation processes, pollutants are completely degraded and destroyed. In these processes, a radiation source (usually ultraviolet light, UV) is used. In heterogeneous catalytic processes, the catalysts are not in the same phase with the reaction medium and can not be easily solved. In order to increase the active surface and reaction efficiency a supportive bed for catalyst would be effective. So, in this study activated carbon made from mango seed has been used as a porous supportive bed with high active surface (10,11).

In a research by Krishna Kumar et al. (2012) entitled "Effect of operating parameters on photocatalytic degradation of Acid Black 1 using zinc oxide as a catalyst", effect of different parameters such as photocatalyst concentration, dye concentration, and initial pH on the efficiency of the process has investigated. The results of this study showed that in the presence of zinc oxide and ultraviolet radiation, 88.4% removal has obtained in 30 minutes. Also, by changing the initial pH from 3 to 7, the removal rate has increased significantly, while at pH>7, the removal rate was significantly reduced (12).

Another study by Muthirulan et al. (2012) entitled "Photocatalytic role of pure carbon coated with zinc oxide in the removal of green alizarin cyanine dye from aqueous solutions" showed that by changing the pH from acidic to neutral and alkaline, the process efficiency declined. The maximum efficiency was obtained in acidic conditions and the minimum efficiency was obtained in alkaline conditions. Also, due to the decrease in ultraviolet penetration and the occupation of the active surface of photocatalyst, the maximum efficiency was obtained at low initial dose of dye (13).

Aims of the study:

Regarding to the fact that removal of dye from wastewater of industries such as textile is indispensable, the aim of this research was to investigate the efficiency of ZnO nanoparticles coated on activated carbon made from mango seed in removing Acid Black 1 from aqueous solutions.

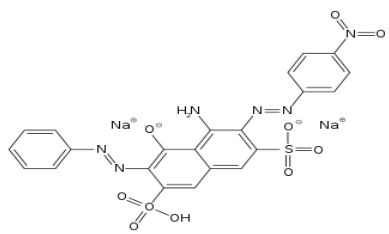
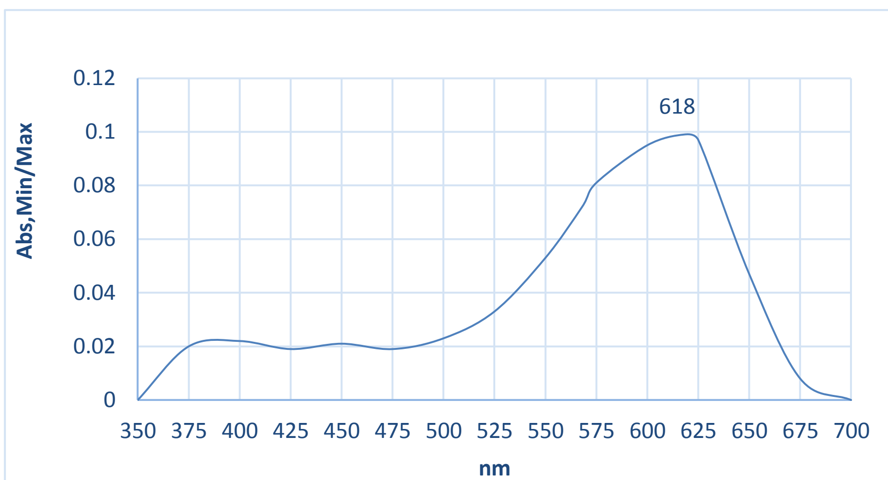
Materials & Methods

This experimental study was carried out in a Photochemical Batch Reactor. Pilot specifications are presented in table 1. The samples were synthetic effluents made in the laboratory with different concentrations of Acid Black 1. The initial pH (3-9), the initial dose of Acid Black 1 (20-200 mg/L), the modified photocatalytic dose (20-100 mg/L) and the reaction time (5-30 min) have investigated. The number of samples was calculated using OFAT (One Factor at a Time Method) and 32 samples were prepared. Acid Black 1 Specifications are presented in table 2

. **Table 1) Pilot specifications**

Type	**Photochemical**
Shape	Cylindrical
Material	Stainless steel
Useful volume	1 Liter
Lamp power	55 watt

Table 2) Acid Black 1 Specifications

Dye Type	**Acidic, soluble, azo dye**
Molecular structure	
Chemical formula	$C_{22}H_{14}N_6Na_2O_9S_2$
Molecular weight	616/49 g/mol^{-1}
Commercial name	Naphthalene Black 10B
Wavelength scan	

Required materials for experiments including Acid Black 1 (99.9% purity) were prepared from the Merck, and Sodium Hydroxide, Sulfuric Acid and ZnO Nanoparticles were prepared from Sigma Aldrich. In this study, the Senoal pH meter (HACH), Sigma centrifuge and DR5000 Spectrophotometer (HACH) were used. Experiments were performed in a batch system by changing pH (3-9), irradiation time (5-30 min), initial dose of Acid Black 1 (20-200 mg/L) and concentration of modified activated carbon (20 -100 mg/L). Samples were taken from the reactor at specified time intervals during the reaction. After preparing the samples, they were centrifuged to remove the catalyst interference on the Detector, and the supernatant was taken for Analysis. Concentration of Acid Black 1 was measured using a DR5000 spectrophotometer at the wavelength of 618 nm (14-16). Data analysis has been done using Excel software. SEM and XRD experiments were conducted to determine the physicochemical characteristics of activated carbon. Acid Black 1 standard concentrations were prepared in the range of 2-50 mg/L from Acid Black 1 standard solution (1000 mg/L) to draw the standard curve by the absorption values. R^2 value of the standard curve for Acid Black 1 was $R^2 > 0.9999$. Also, in every step of the experiment, the removal percentage of Acid Black 1 was calculated using equation (1):

$$\text{Removal } \% = C_0\text{-}C_1/C_0 \qquad (1)$$

C_0: Initial dose of Acid Black 1 in mg/L, C_1: Final dose of Acid Black 1 in mg/L

Modification of produced active carbon via ZnO Nanoparticles:

50 g of dried mango seeds were mixed with a specific volume of 95% phosphoric acid with a mass ratio of 1 to 10. The mixture has been heated in an electric furnace at 900 °C for 1 hour and then the furnace turned off until it reaches ambient temperature. The carbon produced during the above mentioned steps was washed with distilled water until the pH reached to higher than 6.5. After this step, the carbon heated at 120 °C in order to dry it again, after drying, the carbon was grinded and passed through 30, 40 and 50 mesh. Activated carbon modification was carried out by hybrid-mechanical (transplant) method in the above mentioned steps. Various ratios of ZnO to activated carbon at 0.1, 0.2, 0.3 and 0.4 mM/g has been created and analyzed (17-19).

Results

Characterization of Activated Carbon

Characterizations of activated carbon were carried out by SEM and XRD experiments. The results are given in Figures 1 and 2, respectively.

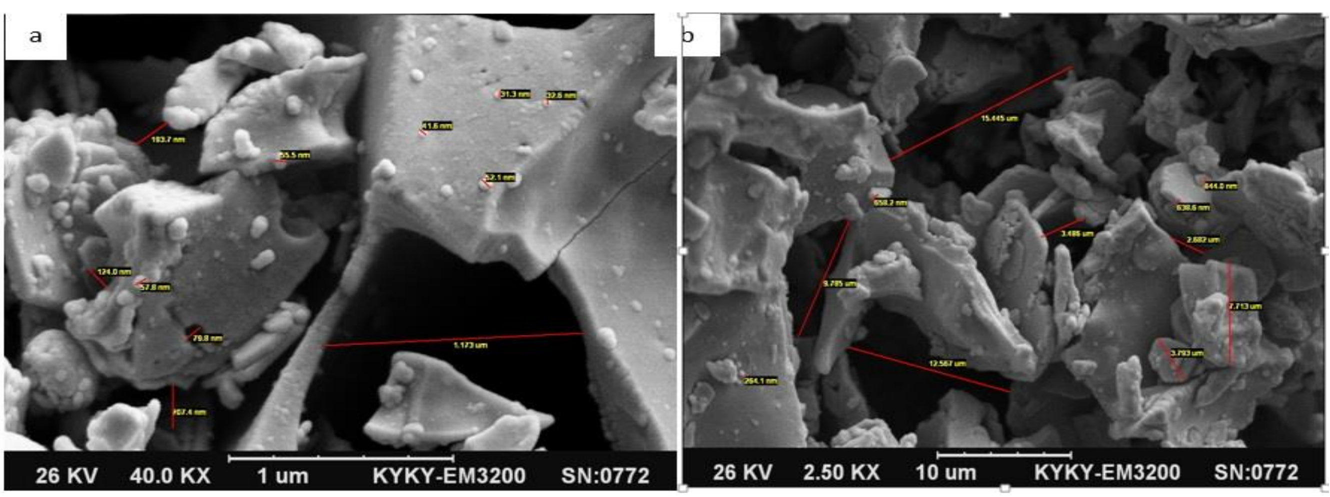


Figure 1) SEM image of activated carbon (a-unmodified b-modified with ZnO)

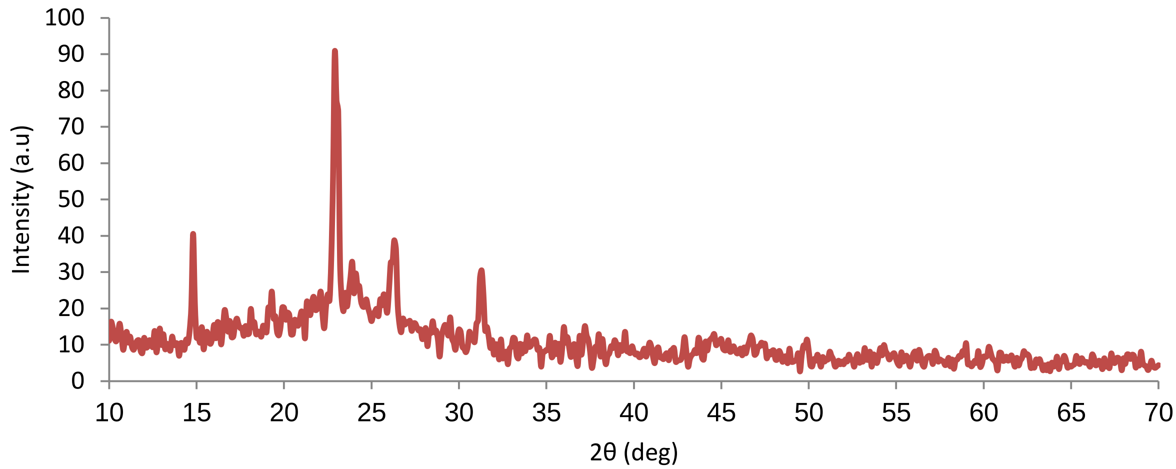


Figure 2) XRD image after modification with ZnO

Effect of pH:

The effect of pH on the removal efficiency is shown in Figure 3. To investigate of pH effect on the process, pH values in the range of 3-9 were studied under constant conditions of modified activated carbon (0.4 molar ratio of ZnO per gram of activated carbon) with concentration of 100 mg/L and the initial dose of Acid Black 1 (100 ppm). The results showed that the maximum efficiency was at pH=3 and the minimum efficiency was at pH=9.

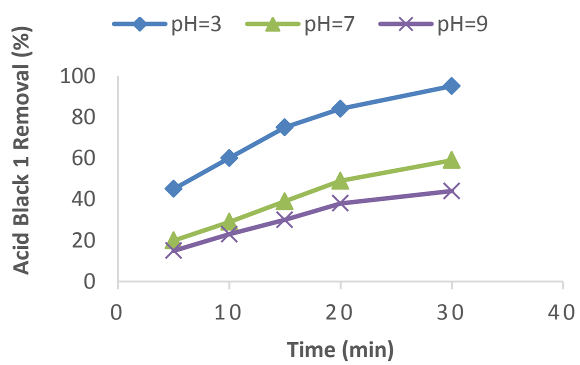


Figure 3) Effect of pH on removal efficiency of Acid Black 1 (modified activated carbon concentration=100 mg/L, initial concentration of Acid Black 1=100 mg/L)

Effect of pure ZnO and ZnO supported with activated carbon:

The results are presented separately in Figure 4. The results showed that efficiency of pure ZnO was lower than ZnO supported with activated carbon in all concentrations.

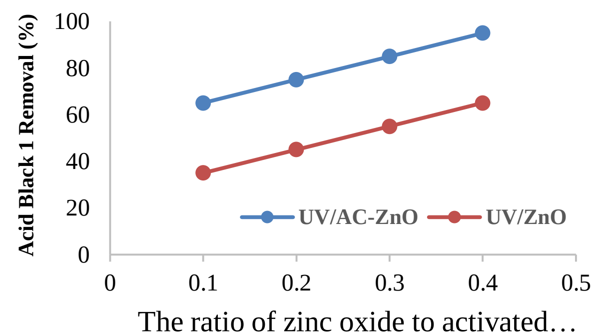


Figure 4) Effect of pure ZnO and ZnO supported with activated carbon concentrations on Acid Black 1 removal (pH=3, initial Acid Black 1 concentration=100 mg/L, Time=30 min)

Effect of initial dose of modified activated carbon:

The effect of modified photocatalyst concentration on Acid Black 1 removal were investigated at of 20, 40, 60, 80 and 100 mg/L concentrations, and the results are shown in Figure 5. The results showed that the maximum efficiency (95%) of the process was at 100 mg/L of modified activated carbon.

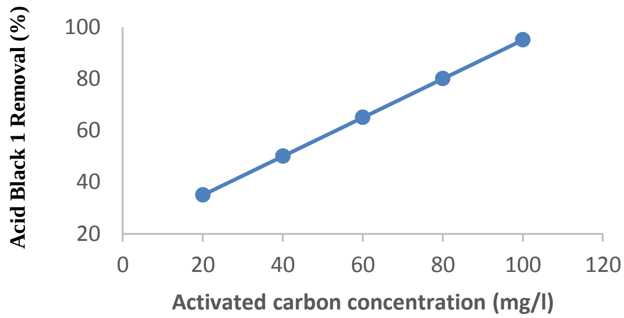


Figure 5) Effect of initial dose of modified activated carbon on Acid Black 1 removal (pH=3, initial Acid Black 1 concentration=100 mg/L, Time=30 min)

Effect of ZNO to activated carbon ratio:

The results of this step are shown in Figure 6. These results showed that by increasing the ratio of ZNO to activated carbon, removal efficiency has increased and in 0.4 mM/g ratio observed efficiency was 95%.

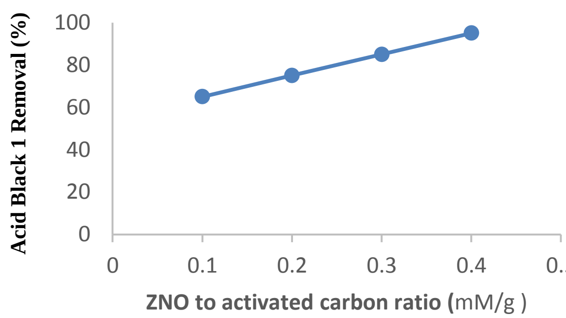


Figure 6) Effect of ZnO to activated carbon ratio on Acid Black 1 removal (pH = 3, modified activated carbon=100 mg/L, initial Acid Black 1 concentration=100 mg/L, Time=30 min)

Effect of initial Acid Black 1 concentration:

At this step, effect of changes in the initial dose of Acid Black 1 has been studied and the results are presented in Figure 7. The results showed that by increasing the initial dose of Acid Black 1, process efficiency has reduced, and the maximum and minimum efficiency was observed at 20 mg/L and 200 mg/L concentrations, respectively.

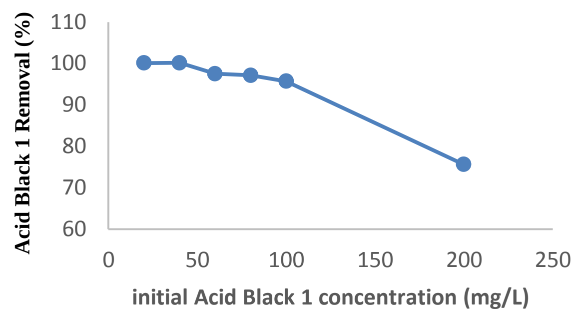


Figure 7) Effect of changes in the initial dose of Acid Black 1 on the process efficiency (pH=3, modified activated carbon=100 mg/L, Time=30 min)

Discussion

Characterization Tests Analysis:

Identifying the structure of modified activated carbon is an important measure to estimate process efficiency. The results of the SEM (Figure 1) showed that the produced activated carbon had a porous structure with a suitable wide surface which could increase the contact between reactants and consequently process efficiency. The results of the XRD (Figure 2) showed that the peak points at 31.6o, 34.2o, 36.2o, 47.4o ranges belonged to zinc oxide (19).

Effect of pH:

pH is the most effective variable in determining the efficiency of chemical processes. pH affects the process efficiency by affecting surface charge. In this study, the maximum system efficiency was obtained in acidic conditions. In acidic conditions, the surface charge of ZNO photocatalysts are positive which causes more Acid Black 1 to be absorbed on the surface, and consequently higher degradation and removal efficiency. In low pH (pH=3) after 30 minutes, the maximum achieved efficiency was 95%. While in alkaline conditions these circumstances are exactly the opposite of acidic conditions, because of negative surface charge of photocatalyst that reduces Acid Black 1 absorption, and consequently reduces the degradation and removal efficiency of process.

In high pH (pH=9) after 30 minutes, the minimum observed system efficiency was 44% which is along with other studies (20,21). In a research by Rahmani et al. (2016), the effect of silica on the ultrasonic/persulfate process for Acid Black 1 removal has been studied. The results showed that in this process, alteration of pH from neutral to acidic and alkaline conditions severely reduces system performance (15). A study by P. Muthirulan et al. (2012) entitled "Photocatalytic role of pure carbon coated with zinc oxide in the removal of green alizarin cyanine dye from aqueous solutions", showed that changing the pH of the solution from acidic to neutral and alkaline conditions decreased the process efficiency, and the maximum and minimum efficiency observed in acidic and alkaline conditions, respectively (13).

Effect of photocatalyst concentration:

The results showed that there is a direct relationship between the photocatalyst concentration and the removal efficiency of Acid Black 1. An increase in the photocatalyst concentration resulted in an increase of active sites on activated carbon's surface, which have increased the absorption of Acid Black 1 and process efficiency. These results are consistent with the study by Kadirova ZC et al. (2013), titled "Photocatalytic degradation and adsorption role of granular activated carbon coated with iron ion to remove methylene blue from saline solutions" (22). Also, the results of a study by Muthirulan et al. (2012) entitled "Photocatalytic role of pure carbon coated with zinc oxide in the removal of green alizarin cyanine dye from aqueous solutions" showed that as the modified catalyst increased, the process efficiency has increased, so that by increasing of modified catalyst concentration to 280 mg/L, the process efficiency has been reached to 95%, which corresponds to the results of the present study (13).

Effect of ZNO to activated carbon ratio:

In this study, as the concentration of ZnO nanoparticles increased, the system efficiency increased. In this process, nanoparticles as a photocatalyst absorbed high-energy photons of ultraviolet spectrum and subsequently released active chemicals such as hydroxyl and peroxide radicals, which play a major role in degradation of the pollutant (22, 23). The results of a study by Samarghandi et al., Titled "Kinetic determination and efficiency of titanium dioxide photocatalytic process in Removal of Reactive Black 5 (RB5) dye and cyanide from aquatic solution", showed that the higher the amount of titanium dioxide photocatalyst were, the higher the process efficiency were, and the maximum efficiency was observed at 1 g/L of photocatalyst concentration (10). Also, the results of present study showed that zinc oxide alone had a lower efficiency compared to ZnO supported with activated carbon. The results of a study by Muthirulan et al. (2012) entitled "Photocatalytic role of pure carbon coated with zinc oxide in the removal of green alizarin cyanine dye from aqueous solutions" showed that the maximum efficiency of pollutants degradation by zinc oxide alone in 90 min was 55%, while for ZnO supported with activated carbon, during the same time, the process efficiency increased by 95% (13).

Effect of initial Acid Black 1 concentration:

The results of this step showed that by increasing the initial dose of Acid Black 1, the removal efficiency decreased. As the initial dose increased, more molecules were absorbed on the surface of the photocatalyst that inhibited the direct contact and reaction of Acid Black 1 with photonic holes and the hydroxyl radicals. It should be noted that the high initial dose in the solution results in more oxidant consumption and increased reaction time. The results of this step are consistent with a study by Rahmani et al. (2016), entitled "the effect of silica on the ultrasonic/persulfate process for Acid Black 1 removal" (15). The results of another study by Muthirulan et al. (2012)

showed that the higher the initial dose of dye was, the lower the process efficiency were, so that at initial dose of 10 mg/l, the efficiency was approximately 100%, while in the same variable conditions and initial dose of 80 mg/l efficiency has reduced to 97% (13).

Conclusion

The results of this study showed that photocatalyst concentration and contact time have a direct correlation with process efficiency in removing Acid Black 1 dye. Also, the process efficiency in acidic conditions is far more than neutral and alkaline conditions. The results showed the high efficiency of ZnO coated on synthetic activated carbon compared to pure zinc oxide.

Footnotes

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This study has been adapted from an MSc thesis at Hamadan University of Medical Sciences. The study was funded by Vice-chancellor for Research and Technology, Hamadan University of Medical Sciences (No. 9610126532).

Conflict of Interest:
The authors declared no conflict of interest.

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