Sigma J Eng & Nat Sci 35 (1), 2017, 61-68

Sigma Journal of Engineering and Natural Sciences
Sigma Mühendislik ve Fen Bilimleri Dergisi

Research Article / Araştırma Makalesi

ANTIBACTERIAL ACTIVITY OF A NANOFILTRATION MEMBRANE FUNCTIONALIZED WITH STABLE TiO_2 NANOPARTICLE SOLUTION PREPARED BY USING NEWLY MODIFIED HYDROTHERMAL METHOD

Aslı ÇOBAN*[1], Eyüp DEBİK[2], Cengiz KAYA[3], Gül KAYKIOĞLU[4]

[1]Bahcesehir University, Faculty of Engineering and Natural Sciences, Besiktas-ISTANBUL
[2]Yildiz Technical University, Environmental Engineering Department, Esenler-ISTANBUL
[3]Yildiz Technical University, Metallurgical and Materials Engineering Department, Esenler-ISTANBUL
[4]Namik Kemal University, Environmental Engineering Department, Corlu-TEKIRDAG

Received/Geliş: 08.12.2016 Revised/Düzeltme: 19.12.2016 Accepted/Kabul: 28.12.2016

ABSTRACT

Stable nanoparticle solution is the key parameter to obtain a uniform coating layer on the membrane surface without any aggregation for an efficient photocatalytic activity. In this study, a commercial titanium dioxide (TiO_2, P25) was used to functionalize the nanofiltration (NF) membrane surface to be able to increase the water disinfection effects of the membrane. A polymer (Polyethyleneimine, PEI) bonding was used to be able to disperse TiO_2 evenly in the solution by using newly modified hydrothermal method. Stability tests were conducted to test the stability of the nanomaterial in suspension. For surface coating, the NF membrane was incubated in contact with the uniform/stable nanoparticle solution. Contact angle measurements were conducted to evaluate the surface characteristic of the functionalized membrane and antibacterial tests were performed to evaluate the water disinfection effects of the functionalized membrane.
Keywords: Nanoparticle, TiO_2, membrane, surface coating, antibacterial activity.

YENİ GELİŞTİRİLEN MODİFİYE EDİLMİŞ HİDROTERMAL YÖNTEM KULLANILARAK HAZIRLANAN STABİL TiO_2 ÇÖZELTİSİ İLE KAPLANAN NANOFİLTRASYON MEMBRANININ ANTİBAKTERİYEL AKTİVİTESİ

ÖZ

Verimli bir fotokatalitik aktivite için membran yüzeyinde herhangi bir çökelme olmadan üniform bir kaplama tabakasının elde edilmesi için stabil bir nanopartikül çözeltisi hazırlayabilmek anahtar parametredir. Bu çalışmada, membranın su dezenfeksiyon etkisini artırabilmek için ticari olarak temin edilen titanyum dioksit (TiO_2, P25) kullanılarak nanofiltrasyon membranı (NF) kaplanmıştır. Yeni geliştirilen modifiye edilmiş hidrotermal yöntem kullanılarak TiO_2'in çözelti içinde homojen bir şekilde dağılmasını sağlayabilmek için polimer (Polyethyleneimine, PEI) bağlama kullanılmıştır. Nanomateryalin çözeltideki stabilitesini analiz edebilmek için stabilite testleri yapılmıştır. Yüzey kaplama için NF membranı üniform/stabil nanopartikül çözeltisinde bekletilmiştir. Kaplanmış membranın yüzey karakteristiğini belirleyebilmek için temas açısı ölçümleri yapılmış olup antibakteriyel testler ile de su dezenfeksiyon özellikleri değerlendirilmiştir.
Anahtar Sözcükler: Nanopartikül, TiO_2, membran, yüzey kaplama, antibakteriyel aktivite.

[*] Corresponding Author/Sorumlu Yazar: e-mail/e-ileti: aslicoban34@yahoo.com, tel: (506) 391 90 05

1. INTRODUCTION

TiO_2 is one of the most known nanoparticles regarding its photocatalysis effect. The main problem in nanomaterial applications is the agglomeration of the TiO_2 nanoparticles. The actual size of commercial TiO_2 nanoparticles (such as P25) is about 20 nm, but its particle size in dispersion could be hundreds of nanometers due to agglomeration [1]. A stable nanoparticle solution is the key parameter to obtain a uniform coating layer on the membrane surface without any aggregation. TiO_2 nanoparticles tend to aggregate in the solution resulting the agglomeration of the TiO_2 nanoparticles on the membrane surface and the low or complete absence of photocatalytic activity [2, 3]. In other words, TiO_2 nanoparticles should be stable and/or well dispersed in the solution to be able to get better photocatalytic activity.

One of the most effective methods to overcome the agglomeration problem of TiO_2 particles is surface modification [2, 3]. Polyethylene imine (PEI) polymer can be used to bond TiO_2 nanoparticles to be able to prepare stable nanoparticle solutions without agglomeration [4]. Dimethylformamide (DMF) can be used as a solvent for bonding TiO_2 with PEI [4]. A strong chemical bond is needed for an efficient membrane surface coating. A covalent bond was tried to be formed between the carboxyl groups of the membrane surface and the amine groups of PEI bonded TiO_2 particles [5].

In this study, a commercial titanium dioxide (TiO_2, P25) was used to functionalize the NF membrane surface to be able to increase the water disinfection effects of the membrane. A polymer (PEI) bonding was used to be able to disperse TiO_2 evenly in the solution by using newly modified hydrothermal method and stability tests were conducted to test the stability of the nanomaterials in suspension. The hydrothermal method which was modified in this study is very simple and convenient for preparing stable nanoparticle solutions. For surface coating, the NF membrane was incubated in contact with the uniform/stable nanoparticle solution. Contact angle measurements were conducted to evaluate the surface characteristic of the functionalized membrane and antibacterial tests were performed to evaluate the water disinfection effects of the functionalized membrane.

2. MATERIALS AND METHODS

2.1. PEI Bonding of TiO_2 Nanoparticles

A commercial titanium dioxide (TiO_2, P25) was used to functionalize the membrane surface for water disinfection. Polyethyleneimine (PEI) bonding was performed to be able to disperse TiO_2 nanoparticles evenly in the solution to get the stable nanoparticles and bind the semiconducter TiO_2 nanoparticles to the membrane surface strongly. Dimethylformamide (DMF) was used as a solvent for bonding TiO_2 with PEI. The PEI bonded TiO_2 nanoparticle solutions having two different concentrations (100 and 500 mg/L) were prepared by using hydrothermal method. The hydrothermal method performed by Kanehira et al. [4] was modified in this study.

0.1% (w/v) TiO_2-DMF and 0.1% (w/v) PEI-DMF solutions were mixed in order to prepare 100 and 500 mg/L of solutions. For 100 mg/L solution 10% of TiO_2-DMF and 90% of PEI-DMF solutions were mixed. For 500 mg/L solution 50% of TiO_2-DMF and 50% of PEI-DMF solutions were mixed. The mixtures were stirred for 12 h. In this newly modified hydrothermal method, 10 mL of PEI-TiO_2 (solvent DMF) solution having the concentration of 100 mg/L was transferred to an erlenmeyer. The erlenmeyer was equipped with a glass reflux to maintain the temperature stable. A stirring hot plate was adjusted to 150ºC and a synthesis reaction was allowed to proceed at 150°C for 6 h. After the completion of the reaction, the solution was cooled at a lower temperature (<50°C). 20 mL of isopropanol was added to the cooled solution. The mixture was allowed to stand at room temperature for 30 min, and the resultant precipitate was collected by centrifugation. The collected precipitate was washed for 3 times with 70% ethanol by centrifugation, and finally 10 mL of deionized water (DIW) was added thereto to prepare a dispersion of the PEI bonded TiO_2 particles. This procedure was repeated for 500 mg/L of solution. The zeta potential and particle size values of the PEI bonded TiO_2 nanoparticles were measured with Zetasizer Nano Device. The success of the newly modified procedure was evaluated considering the zeta potential and particle size results.

2.2. Stability Tests

The stability of the solution is a key factor that affects the homogeneous distribution of the nanoparticles on the membrane surface via surface coating. TiO_2 nanoparticles tend to aggregate in the solution resulting the agglomeration of the TiO_2 nanoparticles on the membrane surface and the low or complete absence of photocatalytic activity [2, 3]. In other words, the TiO_2 nanoparticle should be stable and/or well dispersed in the solution to be able to get better photocatalytic activity with the nanoparticles. One of the most effective methods to minimize the agglomeration of TiO_2 particles is surface modification [2, 3]. In this study polyethyleneimine (PEI) polymer was used to get a stable TiO_2 nanoparticle solution for the membrane surface modification. The stability of the solutions were evaluated using the stability tests as stated in the literature [2, 3, 6-11].

2.3. Membrane Surface Coating and Characterization

A strong chemical bond (covalent bond) was tried to be formed between the carboxyl groups of the membrane surface and the amine groups of PEI bonded TiO_2 particles. In this manner, a nanofiltration (NF) membrane (Microdyn Nadir, NP010) was used which naturally has carboxyl groups on it (Table 1).

Table 1. Microdyn Nadir NP010 membrane characteristics

Brand	Microdyn Nadir
Product Code	NP010
Membrane Type	Nanofiltration
Membrane material	Polyethersulfone (PES)
Molecular Weight Cut-off (MWCO)	10000 Da

NF membrane was cut into circular shape with a 20 mm diameter, incubated in contact with the uniform/stable PEI bonded TiO_2 nanoparticle solutions (100 and 500 mg/L) for 24 h and the change of the surface characterization of the membranes was evaluated. The active sides of the NF membranes were incubated in contact with 4 mL of the PEI bonded TiO_2 nanoparticles for 24 h [12]. After the coating procedure, membranes were rinsed with DIW and contact angle measurements were performed on the membrane surfaces to evaluate the surface characterization of the functionalized membrane.

2.4. Antibacterial Activity

The antibacterial activity of the functionalized membrane was investigated by using inhibition zone method. In this method, TiO_2 coated membrane were irradiated for 1 h under Toplux F8T5/BL (4 lamps, 8W/each) UV light exposure. Afterward the irradiated membrane was placed to an inoculated (*P.aeruginosa*) petri dish in contact with microorganisms. The petri dish is placed to the incubator for 48 h at 37 °C. At the end of the incubation period, bacteria colonies and clear zone formation were observed around the membranes to be able to evaluate the antibacterial activity [13-16].

Antibacterial activity inhibition zone test was conducted using the standard Kirby Bauer approach [14, 17-20]. The membrane coated with the solution of 500 mg/L, which has illustrated better contact angle value, was subjected to the antibacterial activity test under UV light exposure for 1 h. In Kirby Bauer method, P.aeruginosa was spread onto Tryptic Soy Agar plates with a sterile cotton swab from a bacterial suspension having 0.5 McFarland standard. Three membrane samples with the photocatalytic layer facing down in contact with the agar surface were placed onto the petri dish and pressed gently. After incubating at 37°C for 2 days, colonies were observed and digital image of the plate was captured.

3. RESULTS AND DISCUSSION

3.1. PEI Bonding of TiO_2 Nanoparticles

The zeta potential results with 100 and 500 mg/L solutions were +5.09 and +26.5 mV, respectively. The particle size results were 953.3 and 674.2 nm, respectively. High zeta potential value represents the effectiveness of the polymer bonding. It was stated in the literature that +30 mV is a good value for PEI bonded TiO_2 nanoparticles [4]. Having about +30 mV of zeta potential value, it can be said that the 500 mg/L of solution is better than the 100 mg/L of the solution. Furthermore the particle size distribution of the 500 mg/L of solution is better, and this means the solution is homogeneous.

The size results obtained with the modified hydrothermal method can be considered as high. However when they compared with the results in the literature (Table 2), it can be concluded that these results are satisfying. Because the actual size of commercial TiO_2 nanoparticles is about 20 nm, its particle size in dispersion could be hundreds of nanometers due to agglomeration [1]. Table 2 represents the comparison of the different TiO_2 test nanomaterials by means of the particle size and zeta potential results.

Table 2. Comparison of the coated and uncoted TiO_2 test nanomaterials by means of the size and zeta potential measurement results

TiO_2 type	Crystalline form	Coating Material	Particle Size (nm)	Particle size in suspension (nm)	Zeta potential (mV)	Reference
P25	86% Anatase 14% Rutile	Uncoated	21	220	+23	[21, 22]
PC105	Anatase	Uncoated	15-25	560	+29	[21, 22]
M212	Rutile	Coated (Al_2O_3)	20	670-1270	---	[23]
M262	Rutile	Coated (Al_2O_3+Dimetikon)	20	180-720	+26	[21-23]
P25	86% Anatase 14% Rutile	Coated (PEI)	---	674,2	+26,5	In this study

According to the literature it is known that hydrothermally prepared nanoparticles are mostly in the form of anatase and this form is better for photocatalysis [24].

3.2. Stability Tests

For stability tests, just 12 h stirred and hydrothermally prepared solutions were compared. At the end of 4 h, the tubes containing 100 and 500 mg/L solutions were observed by means of homogenity and settling properties. Figure 1 represents the stability test results of the solutions prepared by using just mixing or hydrothermal method.

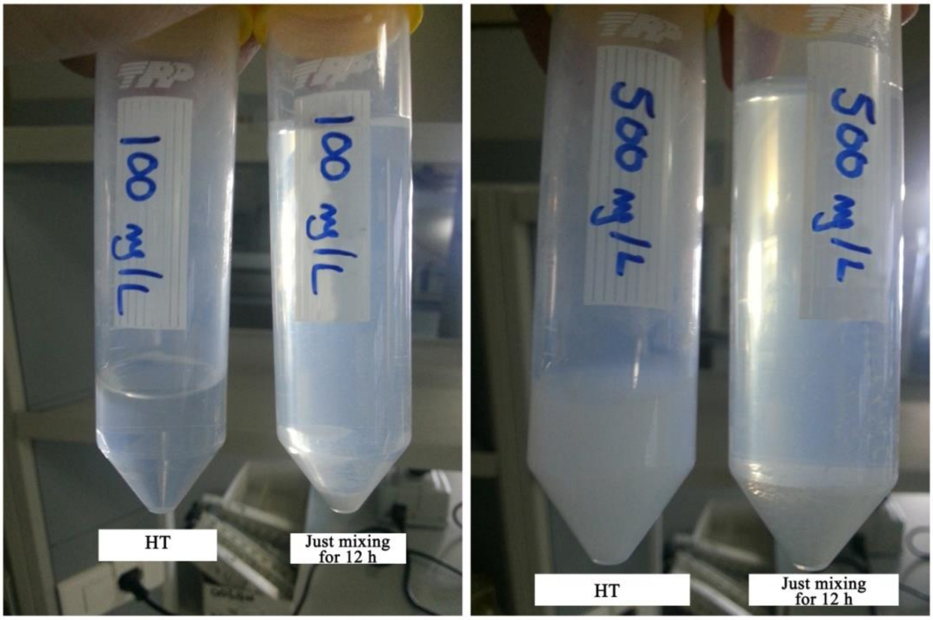

Figure 1. The stability test results of just 12 h mixed and hydrothermally prepared (HT) samples after 4 h of settling test

Once the dispersion stability of bonded particles are lower, particles aggregate and leave a clear supernatant [6]. The obtained results of this study indicated that the hydrothermally prepared samples were more homogeneous than the just stirred ones (Figure 1). The agglomeration and a clear supernatant was observed for the samples prepared by using just stirring method. Based on a study about dispersion stability enhancement, it is clear that untreated TiO_2 particles tend to form large agglomerates within 4 hours in all solvents [2]. Promising results were obtained with this study, consequently it can be pointed that newly modified hydrothermal method which was used in this study is appropriate to obtain stable nanoparticle solutions.

3.3. Membrane Surface Coating and Characterization

Contact angle measurement is a key parameter of the hydrophilicity of the membranes. Table 3 represents the contact angle measurement results for this study.

Table 3. Contact angle measurement results

Sample Name	Contact Angle (°)
Bare (Uncoated) Membrane	67.67
Coated Membrane (solution of 100 mg/L)	66.83
Coated Membrane (solution of 500 mg/L)	53.82

Considering the contact angle measurement results it can be clearly seen that the membrane coated with the solution of 500 mg/L has lower contact angle value. It can be concluded that the coating procedure is successful due to the lower contact angle measurement value of the membrane which represents the hydrophilicity of the membrane [1].

3.4. Antibacterial Activity

The clear zone around the modified membrane indicates the antibacterial properties of the membrane as stated in the literature [13, 14, 16]. Figure 2 indicates the antibacterial effect of the functionalized membrane against P.aeruginosa which has been proven that TiO_2 coated and UV irradiated membrane has the lowest bacteria formation around the membrane.

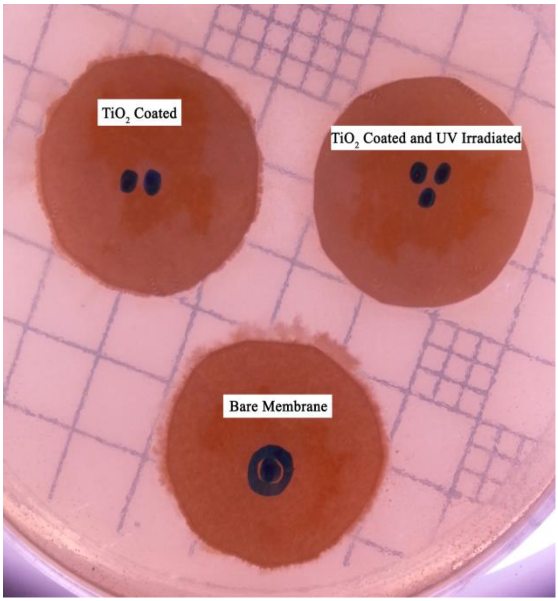

Figure 2. Antibacterial activity test results

The results of this study are satisfying compared to similar studies in the literature [13-16]. These results indicated that the TiO_2 coated and UV irradiated membrane is able to eliminate P.aeruginosa more efficiently than the functionalized membrane with the same concentration of TiO_2 without UV irradiation and bare membrane due to the photocatalytic bactericidal effect of TiO_2 catalyst. Rahimpour et al. [15] stated that the bactericidal effect of UV/TiO_2 photocatalysis is due to the presence of reactive oxygen species generated by TiO_2 or the direct UV irradiation of the cells.

4. CONCLUSION

Contact angle measurements and antibacterial activity test were investigated to be able to evaluate the effects of functionalization on the membrane properties. Contact angle measurements identified that hydrophilicity of the membrane was increased. It means the water flux and antifouling properties of the membrane can be increased by using this surface functionalization. Antibacterial study was performed for the coated membrane and the clear zone around the modified membrane indicated the antibacterial properties of the membrane.

The newly modified hydrothermal method used in this study is simple and convenient way to prepare stable nanoparticle solutions for functionalization of membrane surfaces by means of increasing the antibacterial activity. The results obtained in this study are promising and can be applied for further membrane surface functionalization studies to be able to enhance the antibacterial and antibiofouling activity of membranes.

Acknowledgements / Teşekkür

The study was supported by Yildiz Technical University (Project number: 2013-0502KAP01). Thanks to MEMTEK (National Research Center on Membrane Technologies) for supporting the Zeta Sizer Nano measurements.

REFERENCES / KAYNAKLAR

[1] Chaharmahali A.R., (2012) The effect of TiO_2 nanoparticles on the surface chemistry, structure and fouling performance of polymeric membranes, PhD Thesis, *School of Chemical Engineering*, The University of New South Wales Sydney, Australia.

[2] Kim J.-H., Nishimura F., Yonezawa S., Takashima, M. (2012) Enhanced dispersion stability and photocatalytic activity of TiO_2 particles fluorinated by fluorine gas, *J. Fluorine Chem.*, 144, 165–170.

[3] Rajaeian B., Rahimpour A., Tade M.O., et al., (2013) Fabrication and characterization of polyamide thin film nanocomposite (TFN) nanofiltration membrane impregnated with TiO_2 nanoparticles, *Desalination*, 313, 176–188.

[4] Kanehira K., Sonezaki S., Ogami Y., et al., (2011) Method for Killing Cells Using Photocatalytic Titanium Dioxide Particles, *US Patent 20110060269*, March 10, 2011.

[5] Kang G.-D., Cao Y.-M., (2012) Development of antifouling reverse osmosis membranes for water treatment: A review, *Water Res.*, 46, 584-600.

[6] Boon F., Thomas A., Clavel G., et al., (2012) Synthesis and characterization of carboxystyryl end-functionalized poly(3-hexylthiophene)/TiO_2 hybrids in view of photovoltaic applications, *Synt. Met.*, 162, 1615– 1622.

[7] García-González C.A., Fraile J., López-Periago A., et al., (2009) Preparation of silane-coated TiO_2 nanoparticles in supercritical CO_2, *J. Colloid Interface Sci.*, 338, 491–499.

[8] Tada H., Nishio O., Kubo N., et al., (2007) Dispersion stability of TiO_2 nanoparticles covered with SiOx monolayers in water, *J. Colloid Interface Sci.*, 306, 274–280.

[9] Wang P., Wang J., Wang X., et al., (2013) One-step synthesis of easy-recycling TiO_2-rGO nanocomposite photocatalysts with enhanced photocatalytic activity, *Appl. Catal. B: Environ.*, 132– 133, 452– 459.

[10] Witharana S., Palabiyik I., Musina Z., et al., (2013) Stability of glycol nanofluids — The theory and experiment, *Powder Technol.*, 239, 72–77.

[11] Zhang M., Guiraud P., (2013) Elimination of TiO_2 nanoparticles with the assist of humic acid: Influence of agglomeration in the dissolved air flotation process", *J. Hazard. Mater.*, 260, 122– 130.

[12] Mauter M.S., Wang Y., Okemgbo K.C., et al., (2011) Antifouling ultrafiltration membranes via post-fabrication grafting of biocidal nanomaterials, *ACS Appl. Mater. Interfaces*, 3, 2861–2868.

[13] Li G., Liu H., Zhao H., et al., (2011) Chemical assembly of TiO_2 and TiO_2@Ag nanoparticles on silk fiber to produce multifunctional fabrics, *J. Colloid Interface Sci.*, 358, 307–315.

[14] Liu L., Liu Z., Bai H., et al., (2012) Concurrent filtration and solar photocatalytic disinfection/degradation using high-performance Ag/TiO_2 nanofiber membrane, *Water Res.*, 46, 1101-1112.

[15] Rahimpour A., Jahanshahi M., Rajaeian B., et al., (2011) TiO_2 entrapped nano-composite PVDF/SPES membranes: Preparation, characterization, antifouling and antibacterial properties, *Desalination*, 278, 343–353.

[16] Yang C., Jung S., Yi H., (2014) A biofabrication approach for controlled synthesis of silver nanoparticles with high catalytic and antibacterial activities", *Biochem. Eng. J.*, 89, 10-20.

[17] Bao Q., Zhang D., Qi P., (2011) Synthesis and characterization of silver nanoparticle and graphene oxide nanosheet composites as a bactericidal agent for water disinfection, *J. Colloid Interface Sci.*, 360, 463–470.

[18] Goei R., Lim T.-T., (2014) Ag-decorated TiO_2 photocatalytic membrane with hierarchical architecture: Photocatalytic and antibacterial activities, *Water Res.*, 59, 207-218.

[19] Rizzo L., Della Sala A., Fiorentino A., et al., (2014a) Disinfection of urban wastewater by solar driven and UV lamp - TiO_2 photocatalysis: Effect on a multi drug resistant Escherichia coli strain, *Water Res.*, 53, 145-152.

[20] Rizzo L., Sannino D., Vaiano V., et al., (2014b) Effect of solar simulated N-doped TiO_2 photocatalysis on the inactivation and antibiotic resistance of an E. coli strain in biologically treated urban wastewater, *Appl. Catal. B: Environ.*, 144, 369– 378.

[21] Kuhlbusch T., Nickel C., Hellack B., (2012) Fate and behaviour of TiO_2 nanomaterials in the environment, influenced by their shape, size and surface area, *Environmental Research of the Federal Ministry of the Environment*. Nature Conservation and Nuclear Safety, Project No. (FKZ) 3709 65 417, Report No. (UBA-FB) 001577.

[22] Nickel C., Hellack B., Kuhlbusch T., (2012a) Mobility of three different TiO_2 nanomaterials in soil columns. NanoImpactNet/QNano Presentation, 28.02.2012, Dublin.

[23] Nickel C., Hellack B., Nogowski A., et al., (2012b) Mobility, fate and behaviour of TiO_2 nanomaterials in different environmental media, *Environmental Research of the Federal Ministry for the Environment*. Nature Conservation and Nuclear Safety Chemical and Biological Safety Final Report FKZ (UFOPlan) 3710 65 414.

[24] Sayilkan F., (2007) Synthesis of nano-TiO_2 photocatalyst and determination of its photocatalytic activity, PhD Thesis (In Turkish), *Graduate School of Natural and Applied Sciences*, Inonu University, Malatya, Turkey.