

O 83. PHOTOCATALYTIC Cr (VI) REMOVAL WITH NANOMATERIAL COATED ON NATURAL STONE

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ABSTRACT: Chromium is one of the most common elements in the earth which found in the inner layers of the ground and in the body of living organisms. Certain industrial processes cause serious environmental problems and produce waste streams containing contaminants such as heavy metals. The removal of heavy metal ions, which exhibit a significant toxic effect in wastewater is particularly important in the field of water pollution. Chromium plating, leather tanning, wood shielding and stainless-steel manufacturing industries wastewater mainly contain chromium with valance of 6⁺ and 3⁺. Especially discharging of Cr(VI) to the environment is very dangerous and causes health problems. Therefore, different methods are applied for the treatment of wastewater containing Cr(VI). The most commonly applied methods are reduction of Cr(VI) to Cr(III). Although there are several widely used methods such as chemical precipitation, reduction, dialysis, ion exchange, evaporation, solvent extraction, reverse osmosis and ultrafiltration for Cr(VI) removal in wastewaters, photocatalytic oxidation method has gained great importance in recent periods. In photocatalytic removal, Cr(VI) reduced to Cr(III) with the help of photocatalyst and UV light. In this study, photocatalytic Cr (VI) removal was aimed and Ag and Ni doped TiO₂ nanoparticles were coated on natural volcanic stones as a photocatalyst. Volcanic stones containing Ag and Ni doped TiO₂ (0.5%, 1.0%, 2.5% and 5%) in four different compounds percentages were prepared by sol-gel method. In order to form a solid layer on the natural stone, the coated stones were kept in an oven of 600 °C for 1 hour to produce photocatalyst material and the nanomaterial percentages on the stones were determined by SEM-EDX analysis. Synthetic Cr (VI) containing water was used for removal experiments by using batch reactor. Cr (VI) removal was much higher in the experiment using nanomaterial produced with 0.5% doping. As a result of this study, in water it was determined that the increase in the percentage of Ag and Ni doping has showed a negative effect on the removal of Cr (VI).

Keywords: Chromium, Wastewater, Photocatalyst, Photocatalytic Removal, TiO₂, Ag, Ni.

1. INTRODUCTION

1.1. Chromium Removal Processes

Chromium is one of the most common elements in the earth which found in the inner layers of the ground and in the body of living organisms. The high amount of chromium is found in the iron-containing chromite ore occurring in the magmatic environment. Chromite is the sole commercial source of chromium. When industries go through a certain process, they cause serious environmental problems and produce waste streams containing pollutants such as heavy metals. It is particularly important in the field of water pollution for the removal of heavy metal ions which show significant toxic effects in wastewater. Chromium plating, leather tanning, wood shielding and stainless-steel manufacturing industries wastewater mainly contain chromium with valance of 6⁺ and 3⁺. The discharge of Cr (VI) to the environment is also very dangerous and causes health problems. Hence, various methods are used for the treatment of wastewater containing Cr (VI). The most commonly applied methods are reduction of Cr(VI) to Cr(III). Generally, it is observed that chrome plating, automotive, leather and paint industrial wastes are the main sources of chromium pollution (Balcı, 2019).

Among the methods which are used for the chromium removal from industrial wastewater; chemical precipitation, reduction, dialysis, ion exchange, evaporation, solvent extraction, reverse osmosis, ultrafiltration, flotation, membrane technologies and adsorption are the most commonly used methods. For selecting these methods, the acidic or basic character of the wastewater, the type and concentration

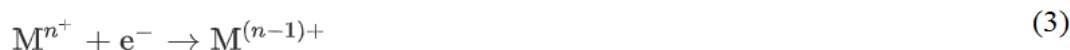
of the chromium compound the content in waste, cost, chemical and energy consumption, management of the new wastes and the efficiency of the wastes are taken into consideration. One of the most commonly used approaches for chromium removal is chemical precipitation. In this method, primarily Cr(VI) ion in the wastewater are reduced to Cr(III), the most stable type of thermodynamics which are using as a reducing agent. (URL 1). The reducing agents used for the reduction of Cr(VI) are salts such as iron(II) sulphate (FeSO₄), sulfur dioxide (SO₂), sodium sulfite (Na₂SO₃) and sodium bisulfite (NaHSO₃) and alkali sulfides. Reduction can be carried out by a reducing agent as well as by light and photocatalyst.

In this study, photocatalytic Cr (VI) removal was aimed and Ag and Ni doped TiO₂ nanoparticles were coated on natural volcanic stones as a photocatalyst. Volcanic stones containing Ag and Ni doped TiO₂ (0.5%, 1.0%, 2.5% and 5%) in four different compounds percentages were prepared by sol-gel method. In order to form a solid layer on the natural stone, the coated stones were kept in an oven of 600 °C for 1 hour to produce photocatalyst material and the nanomaterial percentages on the stones were determined by SEM-EDX analysis. Synthetic Cr (VI) containing water was used for the removal experiments by using batch reactor.

1.2. Photocatalytic Oxidation

TiO₂ is among one of the most important materials in our daily lives. It is widely used in paints, cosmetics and food products. The photocatalytic activity of TiO₂ has helped for further expand of the use of this material.

Photocatalism is called the accelerating of a photoreaction with the presence of a catalyst (Mills and Leunte, 1997). In the semiconductors, the anatase form of TiO₂ shows the highest photocatalytic activity (Hoffmann et al., 1995). Many studies has been done intensively, since this feature of TiO₂ can be a solution to environmental pollution problems. In another aspect of the TiO₂, it is the superhydrophilic property of the surface with the effect of light and this property provides the non-fogging and self-cleaning surfaces. Photocatalytic reactions occur on the surfaces of titanium dioxide thin films. When TiO₂ is stimulated by light, the reaction starts (Şam et al., 2007). The following reactions occur in the photo-reduction of metals:



In eq. (1), when an energy bigger than the band gap of the semiconductor photocatalyst (TiO₂) is given to the fluid distribution of the photocatalyst, the formation of electrons in the conducting band and the opening of the holes in the valence band are indicated. A possible recombination of the electrons produced in eq. (2) and the heat-forming holes which is an unfavorable reaction are indicated. Eq. (3) states that Mⁿ⁺ value any metal ions in the system are reduced by the electrons released in the presence of light. Eq. (4) indicates the oxidation of water. In this study, it is aimed to remove Cr (VI) heavy metal by using modified TiO₂ (Ag and Ni Doped) photocatalyst (Aarthi, 2008).

Cr⁺⁶ is reduced to Cr⁺³ in the presence of UV light and photocatalyst. Experimental conditions such as pH, temperature, photocatalyst properties and organic compounds in the environment are the main factors which can affect the photocatalytic efficiency. During the study, pH and temperature were kept constant and the water used in experiments were synthetically prepared in laboratory. Experiments were performed in the batch system by using TiO₂ photocatalysts which had different percentages.

Nowadays, it has been shown that there are intensive studies on different applications such as heterogenous photocatalysis, hydrogen generation, water and air purification systems and self-cleaning surfaces. Titanium dioxide (TiO_2) is the most useful compound for photocatalytic semiconductor applications due to its high efficiency, low cost, high chemical stability and biocompatibility under ultraviolet light (Mills and Leunte, 1997). During TiO_2 stimulation by ultraviolet light, electron-gap pairs are formed. These electron gap pairs, $\cdot\text{OH}$ radicals and $\text{O}_2\cdot^-$ superoxide produced by the adsorbed to the surface of the photocatalyst causes to oxidize the pollution (Mills and Le Hunte, 1997; Tryk et al., 2000).

In addition to the industrial pollution; it also cause to affect the life of the buildings with the environmental pollution. Another important situation is the pollution of the environment, bacteria, viruses, such as human health in a negative situation, which causes the increasing structures. For this reason, it vital to develop self-cleaning environment-friendly photocatalytic systems that reduce air pollution and decompose bacteria, viruses and toxic organics. For these functions, the photocatalytic feature is provided by the use of anatase TiO_2 powder, while the antibacterial property will provide a permanent antimicrobial effect to the glaze composition, especially Ag, Zn and etc. ions are obtained by adding the appropriate conditions (Gürbüz et. al., 2012).

If the photocatalytic cleavage reaction occurs in the suspension where the catalyst and impurity molecules are in the same location, the change in the amount of catalyst is also observed to change in the photocatalytic activity. Only the maximum amount of the catalyst, the synthesis method of the catalyst on the surface; it is known that it depends on properties such as particle size and surface area and the structure of molecules to be cleaved. As a result, as the amount of catalyst in the environment increases after the known ratio, it is seen that the photocatalytic cleavage rate of the known molecules is increased (Mahmiani, 2016).

Synthesis methods of semiconductor photocatalysts are shown as bellow:

- Sulfate method
- Chloride method
- Micro-plasma oxidation (MPO) method
- Ultrasonic method
- Hydrothermal method
- Sol-gel method

1.3. Sol-Gel Method

The so-called sol-gel process such as soft chemistry is based on the phenomenon of preparing solids from the solution at very low temperature by using the sol or the gel as a medium step which has been observed to date. In fact, it shows the transformation of the sol-gel, hydrolysis and condensation reactions of the molecular precursors of the oxide network. The alkoxide groups in the alcohol and water solution are removed by the hydrolysis in case of acidic or basic catalyst and at the same time hydroxyl groups forming the -M-O-M- bonds are substituted. The gelation indicates that the polymer networks, which continue to grow in order to form the relation indicating the total coverage of the solution are formed. We can see that the viscosity and elastic modulus gradually increase at the time of gelation (Toygun et al., 2013). The gel is then dried by supercritical fluid extraction to evaporate and produce xerogel or to find airogel. It has also been explained that the sol-gel method is a method that can be carried out well under laboratory conditions and the use of the applied method in large-scale production increases day by day.

The basic steps of sol-gel method are as bellow:

- 1- Hydrolysis
- 2- Alcohol or water condensation
- 3- Gelling moment
- 4- Aging moment
- 5- Drying process
- 6- Application of high temperatures process

Sol-Gel method and TiO₂ also used in the synthesis of semiconductor. As the starting material metal alkoxides are used in almost all studies and the basic state of the reaction is known to occur in the hydrolysis and condensation reactions of metal alkoxides in the catalytic medium at 25 °C at room temperature.

The applied method is as:

- 1) To be able to work at a very low temperature,
- 2) Possibility to use organic solvents,
- 3) By using liquid solutions of pure substances homogeneity at molecular levels can be ensured,
- 4) Providing low temperature to produce hydrolysis and condensation reactions, thus avoiding losses that can be observed by evaporation at very high temperatures,
- 5) In experimental studies, even though many other advantages such as being able to be formed with simple glass materials under atmospheric conditions have been observed, the demerits of semiconductors used in photocatalysis reactions are the disadvantages of using their targets as roughness. The gel material formed at the end of the hydrolysis and condensation reaction is a product having a metal alkoxide oxide hydroxide structure.

The conversion of the product to TiO₂, which is the most widely used anatase in photocatalytic studies, must also be dependent on the calcination procedure such as at temperatures too high at oxygen atmosphere e.g; above 450 °C. As the produced substance cannot form a polar or apolar group at random on its surface, it can also be considered as pure TiO₂ in powder form. Only in such cases, after the photocatalysis process has been carried out in the solution phase, the measurements to be made should be separated from this environment by filtration. After every other measurements, it should be applied again. Once the separation from the medium has taken place, the reduction of the surface properties of the catalyst can be seen from the initial dimension, if the surface characteristic of the catalyst may vary. Thus, it will be evident that significant changes in photocatalytic activity will occur.

Nowadays in conducted studies, photocatalytic thin films have attracted considerable influence and attention has been paid to this area in almost every study. The important problem in the films produced is that the surface to be used in the coating process provides the coating solutions and TiO₂, which will exhibit photocatalytic activity to form transparent sols. The TiO₂ particles synthesized by the sol-gel method, as described in previous do not show on the surface of the polar/apolar groups which play a significant role in the formation of the transparent sols. According to Mahmiani. (2016), it has been reported that perhaps the sol of these particles is not produced or sols are not transparent.

2. MATERIAL AND METHOD

2.1. Preparation of Ag-Ni Doped TiO₂ Photocatalyst on a Volcanic Stone

The Procedure of Experiment: In this method, TiO₂ nano-material is first obtained for doping and then the desired metals are doped onto TiO₂ with the help of other solution. Therefore, the aim here is to prepare two different sols. The molar ratios used during the preparation of these sols are given below. The unassembled TiO₂ was obtained by preparing only the sol A.

Sol A: (Ti((OC₄H₉)₄):1-butanol:2-propanol: pure water:acacH = 1:7:3:4:0.5).

Sol B: (ethanol: Ni₂(NO₃)= 20: 1, ethanol: AgNO₃=20:1).

- For preparation of Sol A Titanium butoxide and acetyl acetone were dissolved in 1-butanol.
- The prepared solution was stirred.
- Then the required amount of water was dissolved in 2-propanol and added to the other solution.
- While preparing the sol A, sol B containing Ag and Ni at the planned concentrations was prepared with ethanol. (0.5%, 1.0%, 2.5% and 5% - percentages of AgNO₃ and Ni₂(NO₃) according to titanium precursor [Ti((OC₄H₉)₄)).
- Sol B is added into Sol A and stirred certain time together.
- The obtained sol was ready for the coating process. (Figure 1)

For the volcanic stones, pre-sieving was performed. These stones were then again cleaned with propanol and passed through pure water and dried in the ash oven (Figure 2). The drying process was expected

while preparing the sol without performing the removal into the sol. The volcanic stones (determined by the sieve of their size) were thrown into the sol and waited for 2 minutes. After these processes, they were dried in a desiccator at room temperature for 1 hour (Figure 3). It subjected to heat process to achieve solidification. The synthesized material was kept at 600 °C for 1 hour and the photocatalysts were prepared (Figure 4). The percentages of Ag, Ni and Ti, which were fixed on the prepared material, were determined by EDX analysis.



Figure 1. Mixing process



Figure 2. Drying of volcanic stones in ash oven



Figure 3. Drying process in desiccator



Figure 4. Ag-Ni TiO₂ coated volcanic stones

2.2. Photocatalytic Cr⁺⁶ Removal Experimental Procedure

In the first step, a water sample containing synthetic chromium was prepared. For this purpose, a Cr solution was prepared in the laboratory and diluted with distilled water to a concentration of 5 mg/L and adjusted to a volume of 500 mL. The pH of the prepared solution was brought to about 2.4 by adding 0.1 ml H₂SO₄. To determine the inlet concentration, 1 mL of this solution was diluted 1/5 and measured using the LCK 313 cuvette test (Figure 5). Volcanic stones of 15 gr weight were thrown into the prepared sample and then mixed (Figure 6). In order to bring the system to equilibrium, stirring was performed in dark environment for 15 minutes. At the end of this period, 11W UV light was turned on and photocatalytic reactions were expected to be completed (Figure 7). The system was operated intermittently and the total waiting time reported as 5 hours. Samples were taken from the system at 90,180,240 and 300 minutes and Cr(VI) measurements were made. The parameters considered during the experiments are given in Table 1.



Figure 5. LCK 313 Chrome cuvettes

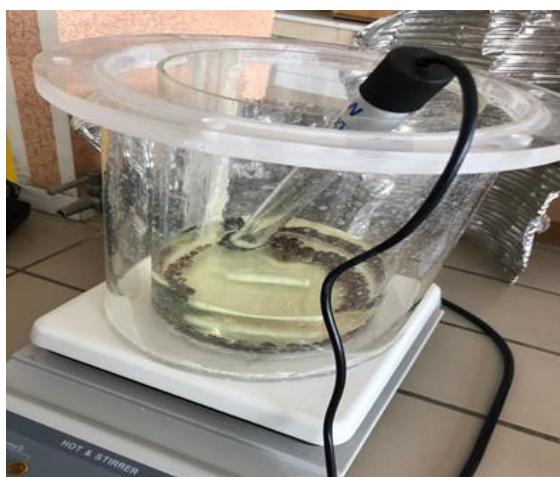


Figure 6. The batch reactor before closing



Figure 7. Mixing in batch reactor with UV light

Table 1. Parameters which set during the experiments

Photocatalyst	Sample Volume (ml)	pH	Photocatalyst Weight (gr)	Mixing velocity (rpm)	Temperature (°C)
0.5% Ag-Ni TiO ₂	500	2.40	15	30	25
1% Ag-Ni TiO ₂	500	2.43	15	30	25
2.5% Ag-Ni TiO ₂	500	2.41	15	30	25
5% Ag-Ni TiO ₂	500	2.42	15	30	25
Non-doped TiO ₂	500	2.43	15	30	25

3. RESULTS AND DISCUSSION

3.1. Material Properties

The retention percentages of Ag, Ni and Ti on the prepared photocatalyst were determined by SEM-EDX analysis. SEM-EDX result graphs obtained by changing the doping percentages are given in the

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following figures (Figure 8, Figure 9, Figure 10 and Figure 11). By evaluation of the obtained results, it was seen that adding more amount of AgNO_3 and $\text{Ni}_2(\text{NO}_3)_6$ in doping process did not affect adherence efficiency very much and it increased regionally Ag and Ni ratio. In particular, it is clear from the results that the adsorption of Ni increases as the doping percentage increases. Since the material structure is amorphous, it is not possible to get closer to the surface, only the elemental percentages of substances added on the stone can be examined. It is understood from the obtained results that the material obtained as the result of this study has nano properties and contains Ag, Ni and TiO_2 . EDX result graph of 0.5% Ag and Ni doped material is illustrated in Figure 8.

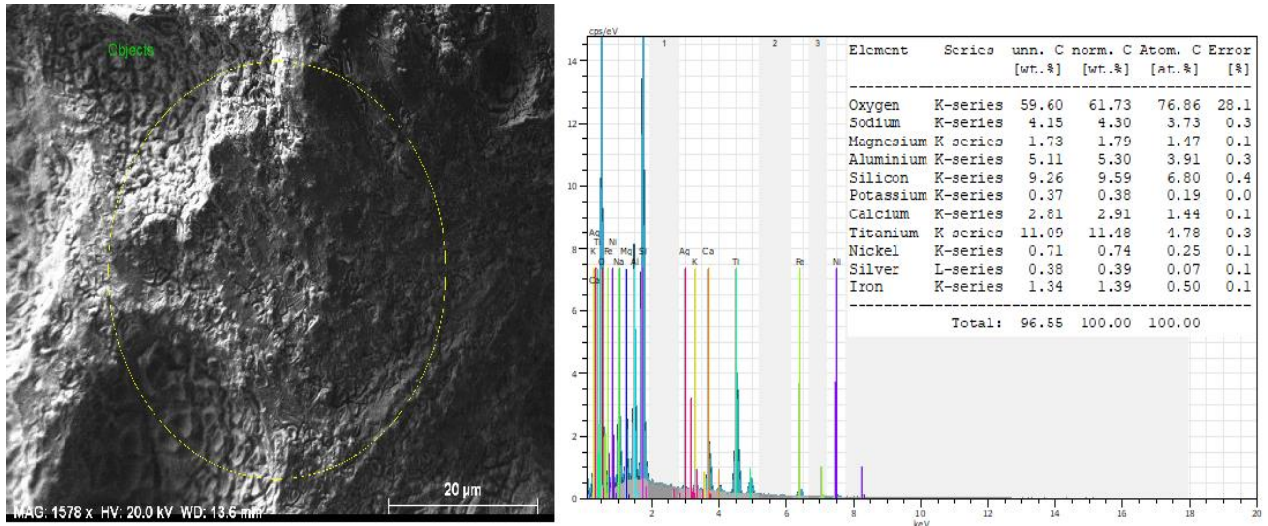


Figure 8. EDX result graph of 0.5% Ag and Ni doped material

EDX result graph of 1.0% Ag and Ni doped material is shown in Figure 9.

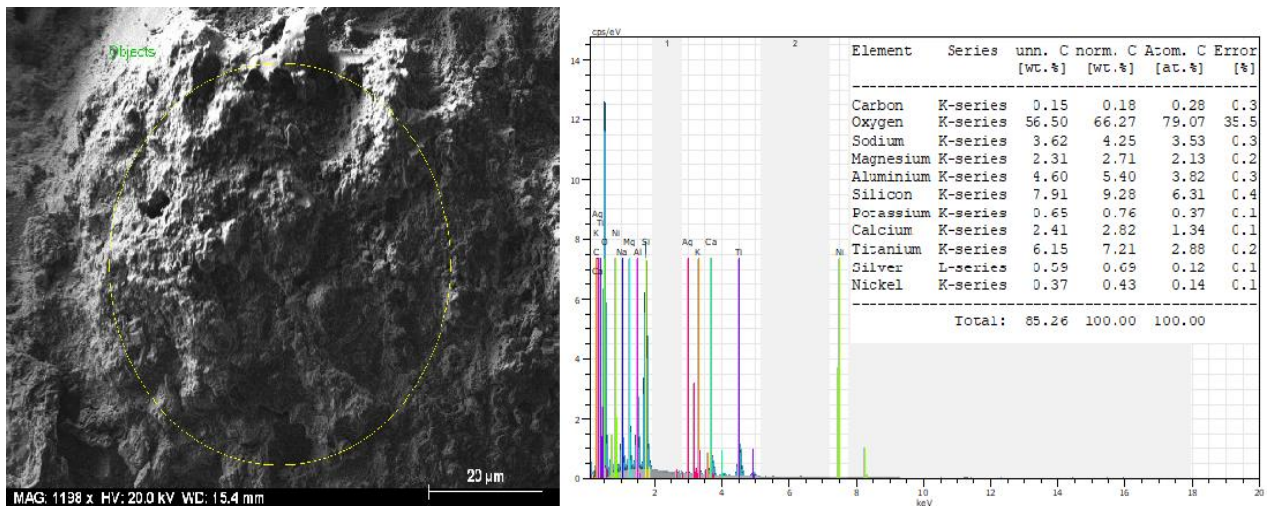


Figure 9. EDX result graph of 1.0% Ag and Ni doped material

EDX result graph of 2.5% Ag and Ni doped material is illustrated in Figure 10.

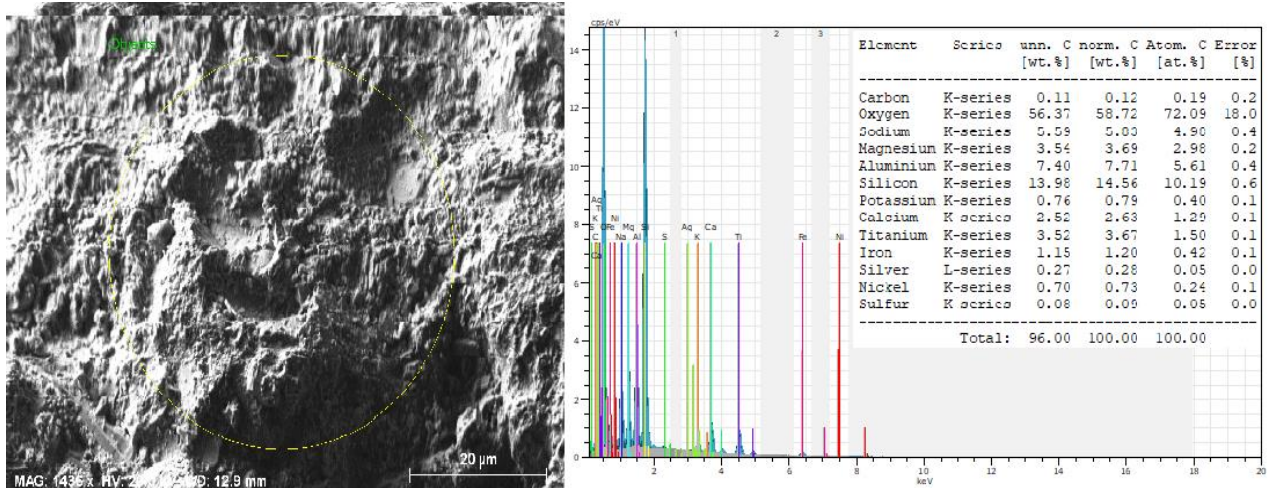


Figure 10. EDX result graph of 2.5% Ag and Ni doped material

EDX result graph of 5% Ag and Ni doped material is illustrated in Figure 10.

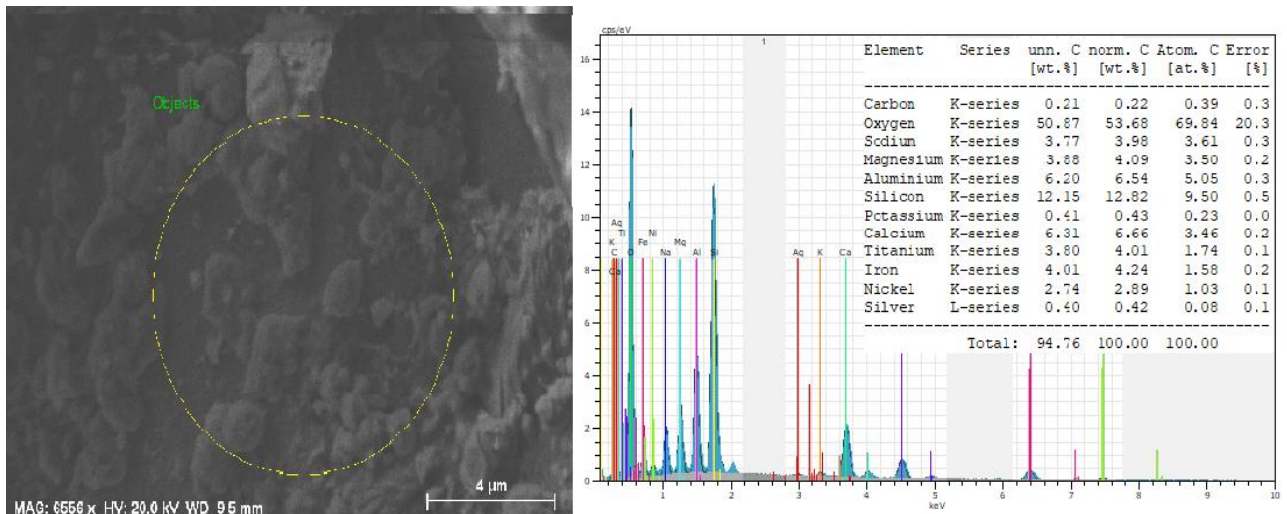


Figure 11. EDX result graph of 5.0% Ag and Ni doped material

3.1. Photocatalytic Cr (VI) Removal

The Cr⁶⁺ concentrations obtained from the conducted experiments during the study are given in Table 2.

Table 2. Concentrations of Cr⁶⁺ obtained from experiments

Time (minute)	0.5% Ag-Ni TiO ₂ (mg/l)	1.0% Ag-Ni TiO ₂ (mg/l)	2.5% Ag-Ni TiO ₂ (mg/l)	5.0 % Ag-Ni TiO ₂ (mg/l)	Non-doped TiO ₂ (mg/l)
C _{inlet}	4.31	5.15	5.80	6.55	7.10
C ₉₀	3.73	4.55	4.65	6.05	5.75
C ₁₈₀	3.27	3.89	4.27	5.45	5.20
C ₂₄₀	2.34	3.27	3.50	5.15	4.83
C ₃₀₀	1.54	2.93	3.17	4.51	4.45

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The removal efficiencies of the samples were calculated from the eq. (5):

$$\text{Removal efficiency} = \frac{C_{inlet} - C_t}{C_{inlet}} * 100 \quad (5)$$

Table 3 shows the removal efficiencies obtained from these experiments. The plotting efficiency graphs for the nano-material coated volcanic stones used in the experiments are given in Figures 12-16. Figure 17 shows the obtained yield graphs all together.

Table 3. Cr⁺⁶ removal yields obtained from experiments

Samples	Efficiency after 90 min (%)	Efficiency after 180 min (%)	Efficiency after 240 min (%)	Efficiency after 300 min (%)
0.5% Ag-Ni TiO ₂	13.47	24.04	45.80	64.23
1.0% Ag-Ni TiO ₂	12.00	25.00	24.04	43.20
2.5% Ag-Ni TiO ₂	20.00	26.50	40.00	45.40
5.0% Ag-Ni TiO ₂	7.60	16.80	21.40	31.22
Non-doped TiO ₂	19.01	27.00	32.00	37.40

Plotted removal efficiency versus time which obtained in the experiment using 0.5% Ag-Ni TiO₂ coated volcanic stone is illustrated in Figure 12.

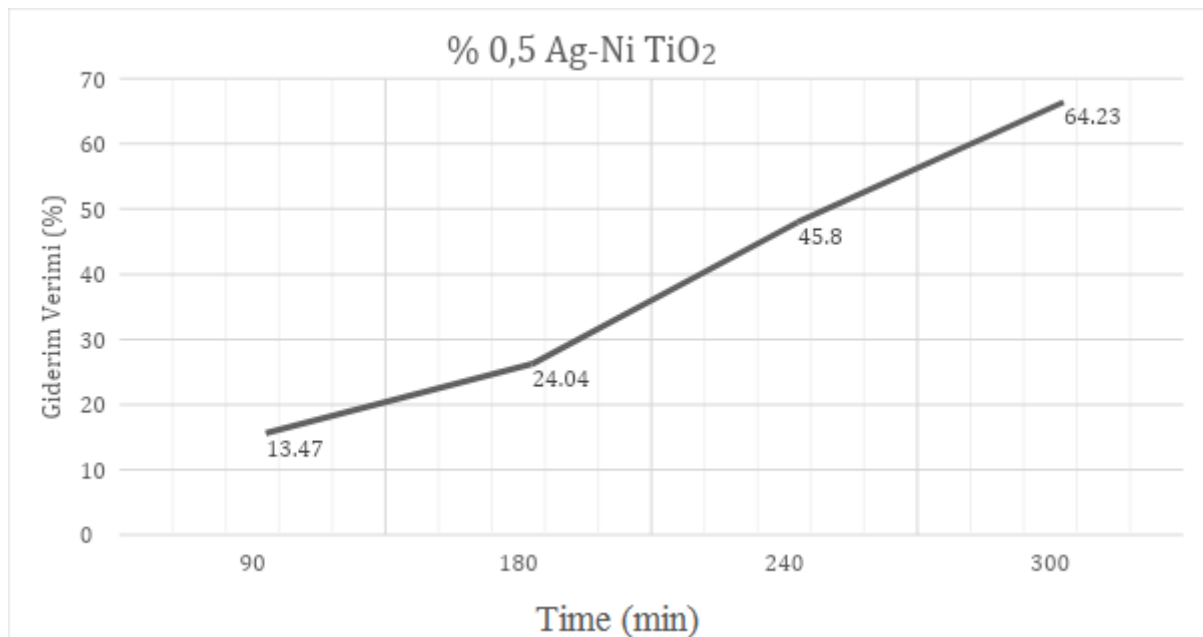


Figure 12. Plotted removal efficiency versus time which obtained in the experiment using 0.5% Ag-Ni TiO₂ coated volcanic stone

Plotted removal efficiency versus time which obtained in the experiment using 1.0% Ag-Ni TiO₂ coated volcanic stone is illustrated in Figure 13.

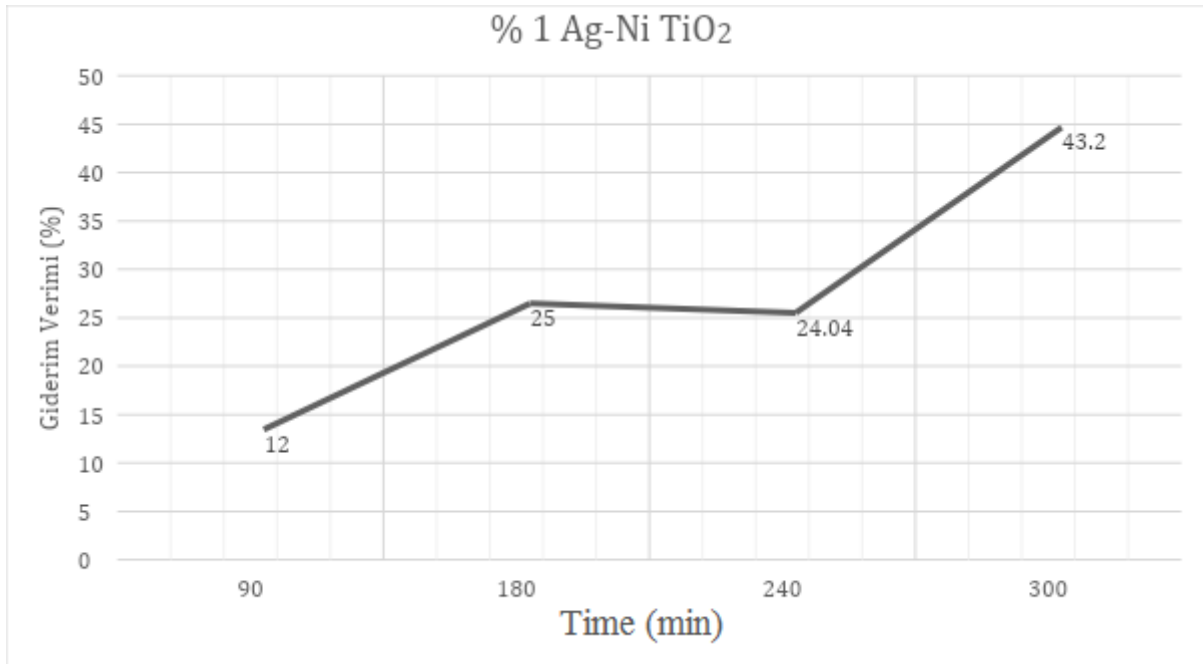


Figure 13. Plotted removal efficiency versus time which obtained in the experiment using 1.0% Ag-Ni TiO₂ coated volcanic stone

Plotted removal efficiency versus time which obtained in the experiment using 2.5% Ag-Ni TiO₂ coated volcanic stone is shown in Figure 14.

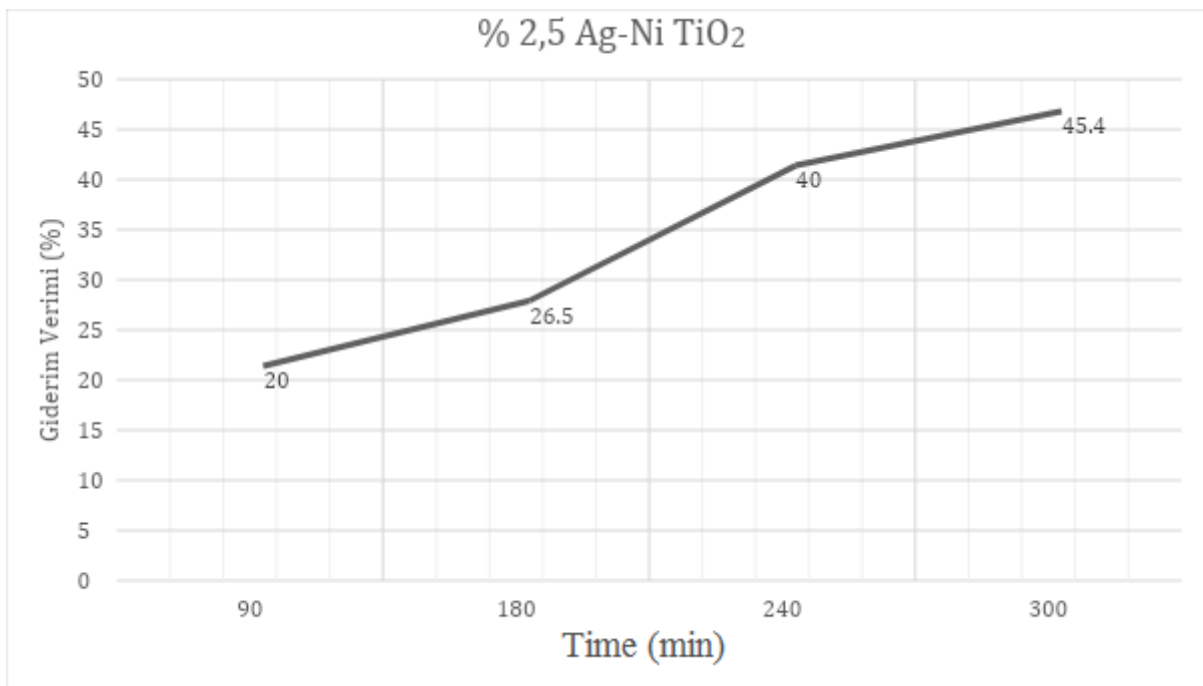


Figure 14. Plotted removal efficiency versus time which obtained in the experiment using 2.5% Ag-Ni TiO₂ coated volcanic stone

Plotted removal efficiency versus time which obtained in the experiment using 5.0% Ag-Ni TiO₂ coated volcanic stone is illustrated in Figure 15.

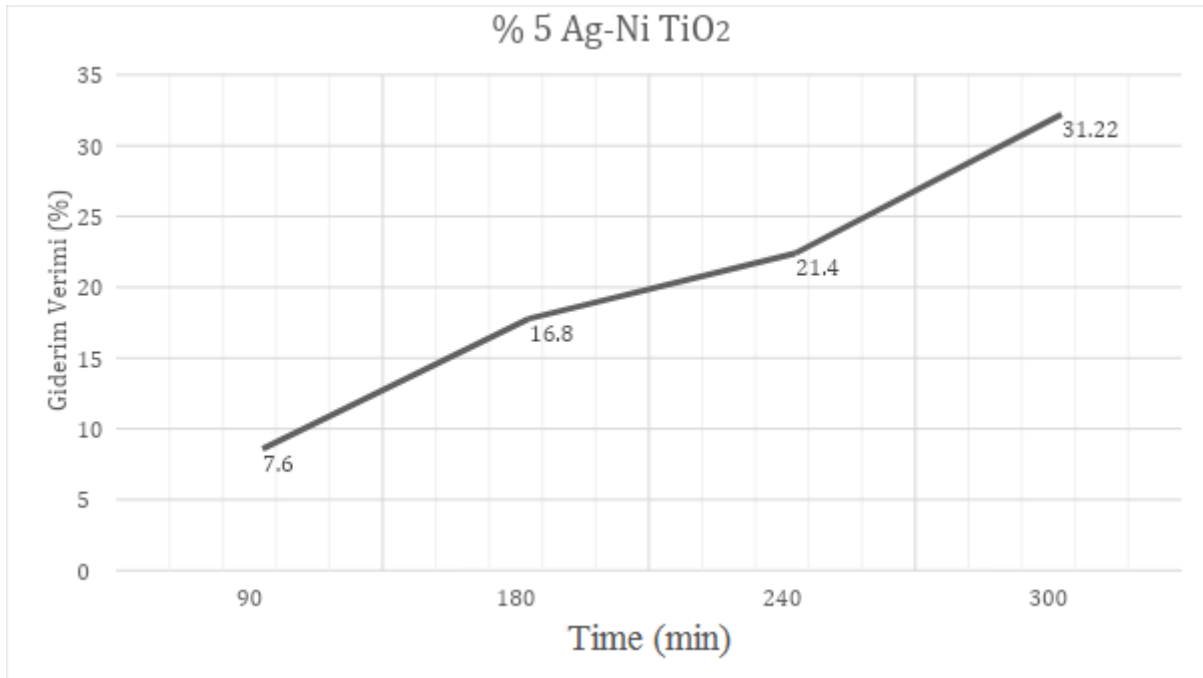


Figure 15. Plotted removal efficiency versus time which obtained in the experiment using 5.0% Ag-Ni TiO₂ coated volcanic stone

Plotted removal efficiency versus time which obtained in the trial using non-doped TiO₂ coated volcanic stones is shown in Figure 16.

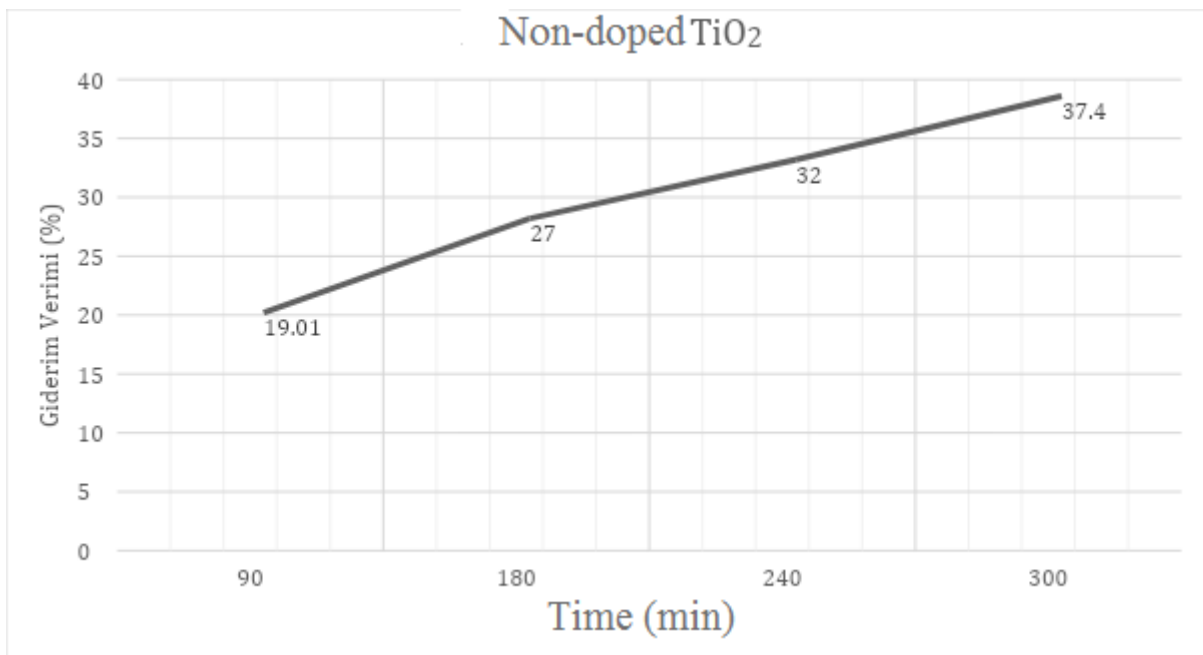


Figure 16. Plotted removal efficiency versus time which obtained in the trial using non-doped TiO₂ coated volcanic stones

Removal efficiency versus time graph is shown with all materials used in the experiments is illustrated in Figure 17.

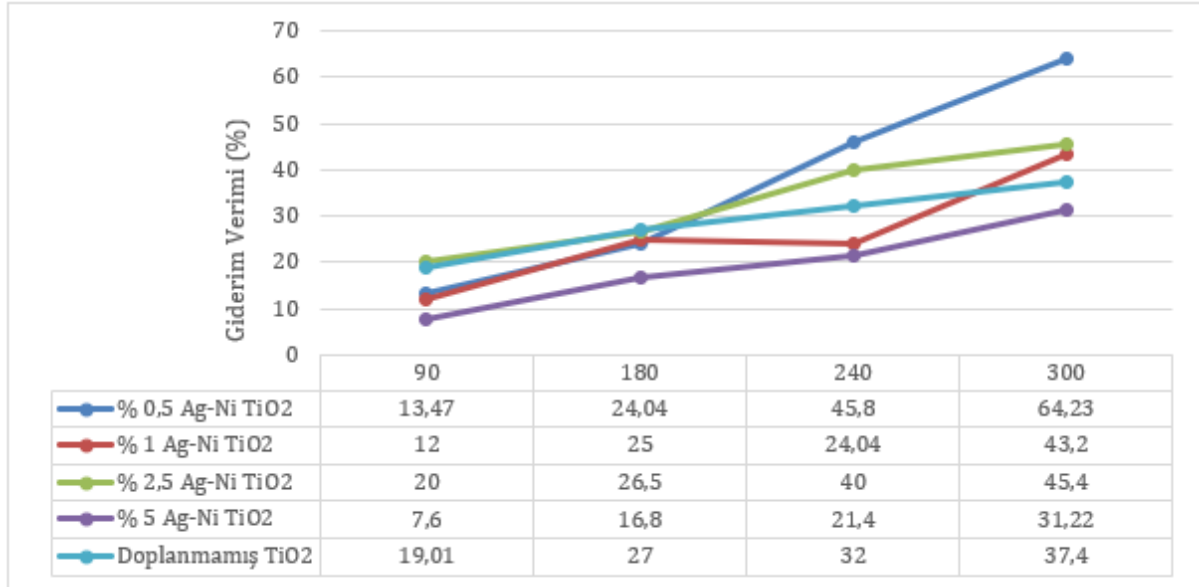


Figure 17. Removal efficiency versus time graph is shown with all materials used in the experiments

The obtained results in this study were evaluated, the highest removal efficiency was obtained by using TiO₂ coated volcanic stones with 0.5% Ag and Ni doping. Increasing the doping percentage was found to slightly reduce Cr(VI) removal. By exploring the literature it was determined that the efficiency increased in the Ag doped studies and no Ni related sample was found. In this study, it is seen that the percentage of doping increases Ni adherence, so Ni is more likely to be the parameter that negatively affects removal efficiency. Further reduction in the yield using TiO₂ obtained without doping proves that doping has a positive effect on efficiency. As a result, it is a logical solution to make Cr⁺⁶ removal in the wastewater with the correct adjustment of the optimum percentage to be doped with photocatalytic methods that are more environmentally friendly and do not produce additional waste.

4. CONCLUSION

In this study, photocatalytic oxidation of Cr (VI) removal is intended by photocatalytic expense in Cr(VI) to Cr(III) wherein the reduction process is done using a photocatalyst and UV light. Ag and Ni doped TiO₂ nanoparticles were coated on natural volcanic stones for use as photocatalysts. Volcanic stones containing Ag and Ni doped TiO₂ (0.5%, 1%, 2.5%, 5.0%) and non-doped TiO₂ in four different percentages were prepared by sol-gel method. For the solution of nano material to form a solid layer on natural stones, the coated stones were kept in 600 °C ash oven for 1 hour and photocatalyst material production was achieved and the percentages of adhesion on the material were determined by SEM-EDX analysis. Synthetically prepared Cr(VI) containing water removal experiments were carried out by using the batch system. It was found that the yield and the removal were not good as the Ag and Ni doping percentage on the volcanic stones used during the experiments increased. In the experiment with non-doped TiO₂ coated stones much lower yield was obtained than the doped TiO₂ coated material of 0.5%. It was found that the high percentage of material doped on TiO₂ had a negative effect on Cr(VI) removal in water while doping had a positive effect. It is possible to achieve higher yields by using a material set at lower levels of doping and by increasing the amount of photocatalyst material which are used.

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