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ARAŞTIRMA MAKALESİ / **RESEARCH ARTICLE**

PHOTOCATALYTIC PERFORMANCE OF TiO_2 COATED CERAMIC TILES

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ABSTRACT

In this work, commercially available titanium dioxide (TiO_2, 25nm) and Si-modified TiO_2 nanoparticles have been deposited on ceramic tiles by spray coating method to product photocatalytic active surface. Phase analyses of the powders and microstructure of the photocatalytic surfaces were characterized with X-ray diffraction method (XRD) and scanning electron microscopy (SEM) respectively. In order to evaluate the photocatalytic activity of the uncoated, unmodified TiO_2 coated and Si-modified TiO_2 coated tiles, methylene blue was used as organic pollutants for the photocatalytic experiments. Thus, methylene blue aqueous solutions were prepared in 5mg/L, 15mg/L and 30mg/L concentrations by dissolving the dye in distilled water. All polluted tiles were placed under direct sunlight irradiation for 120min. Color values of the tiles were recorded by CIE (L,a,b) colorimetric standard system for before photodeposition, after pollution and after photodeposition. The results revealed that, Si-modified TiO_2 coated tiles have shown better photocatalytic activities than uncoated and unmodified TiO_2 coated tiles. It showed that, nearly 100% cleanability degree were observed for Si-modified TiO_2 coated tiles in 80, 100 and 120 min for 5-15 and 30mg/L methylene blue concentrations respectively. On the other hand no completely cleaning was detected for uncoated and unmodified TiO_2 coated tiles for all methylene blue concentrations.

Keywords: Titanium dioxide, Photocatalytic, Ceramic tile, Methylene blue.

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TiO_2 KAPLI SERAMİK KAROLARIN FOTOKATALİTİK PERFORMANSI

ÖZ

Bu çalışmada ticari ve Si ile modifiye edilmiş TiO_2 nanopartükülleri sprey kaplama yöntemi kullanılarak seramik karolar üzerine fotokatalitik yüzey elde etmek amacıyla kaplanmıştır. Tozların faz analizleri ve fotokatalitik yüzeylerin mikroyapıları sırasıyla X-ışınları kırınım metodu (XRD) ve taramalı elektron mikroskobu (SEM) kullanılarak karakaterize edilmiştir. Kaplanmamış, modifiye edilmemiş TiO_2 ile kaplanmış ve Si katkılı TiO_2 ile kaplamış karoların fotokatalitik aktivitesinin incelenmesi amacıyla fotokatalitik deneylerde organik bir kirletici olan metilen mavisi kullanılmıştır. Bu amaçla konsantrasyonu 5mg/L, 15mg/L ve 30mg/L olacak şekilde metilen mavisi saf su içesinde çözündürülerek metilen mavisi içeren solüsyonlar hazırlanmıştır. Tüm kirletilmiş karolar direk gün ışığı altında 120 dakika ışımaya bırakılmıştır. Karoların renk değerleri ışıma öncesi, kirletme sonrası ve ışıma sonrasında kolorimetrik standart sisteme CIE (L,a,b) göre incelenmiştir. Elde edilen sonuçlar Si ile modifiye edilmiş TiO_2 kaplı karoların kaplanmamış ve modifiye edilmemiş TiO_2 kaplı karolara göre daha yüksek fotokatalik aktiviteye sahip olduğunu göstermiştir. Si ile modifiye edilmiş tozla kaplı karoların 5mg/L, 15mg/L ve 30mg/L metilen mavisi konsantrayonlarında sırasıyla 80-100 ve 120 dakika bekleme süreleri için neredeyse 100% temizleme derecesine sahip olduğu gözlenmiştir. Diğer taraftan kaplanmamış ve modifiye edilmemiş TiO_2 ile kaplı karoların her bir metilen mavisi konsantrasyonlarında tamamen temizleme sağlamadığı belirlenmiştir.

Anahtar Kelimeler: Titanyum dioksit, Fotokatalitik, Seramik karo, Metilen mavisi.

1. INTRODUCTION

Photocatalysts such as ZnO, TiO_2 are widely used to decompose organic contaminants due to their strong oxidizing ability (Rego et al, 2009). TiO_2 is well known photocatalytic material due to its high photocatalytic activity, strong oxidative power, photocorossion, photostability, low cost and non-toxicity. Therefore, many researcher have concentrated on the preparation and characterization of nanocrystalline TiO_2 in photocatalyst, solar energy cell, ductile ceramic, gas sensor, mesoporous membrane, and pigment applications (Lin et al, 2007; Yang et al, 2005). TiO_2 has three polymorphs which are brookite, anatase and rutile. The optical energy band gap of anatase and rutile are 3.2 eV (380nm) and 3.0 eV (410nm), respectively. Among them anatase based TiO_2 photocatalyst has better photocatalytic effect than rutile phase. Nearly 5% of solar spectrum can be utilized in photocatalytic application. Thus, several authors have focused on to extend the light responsible range of TiO_2 from the ultraviolet to the visible light region. On the other hand, nanostructured (<100nm) anatase phase can be transformed into the rutile phase at above 600 ^oC (Kim et al, 2005; Su et al, 2008). Therefore, many studies has been published that Al_2O_3/TiO_2, ZrO_2/TiO_2, SnO_2/TiO_2, SiO_2/TiO_2 mixed oxides shows more excellent photocatalytic activity than pure TiO_2. Among them addition of SiO_2 provides both high photoactivity and anatase phase stability at above 600 ^oC (Xu et al, 2009). On the other hand, application and photocatalytic performance of Si modified TiO_2 coated ceramic tiles have not been published for various methylene blue concentrations. In this study, the objectives are modification of TiO_2 with Si to enhance phase transition of the TiO_2 particles, and also to compare photocatalytic efficiency of uncoated and Si modified TiO_2 coated tiles for 5mg/L, 15mg/L and 30mg/L methylene blue concentrations.

2. METHODS

In order to deposit photocatalytic surface, commercially available TiO_2 nanoparticles (25nm, 80/20 anatase/rutile) were selected.

Tetraethylorthosilicate (TEOS) were used for preparation of Si modified TiO_2 nanoparticles. Unmodified and Si modified TiO_2 nanoparticles were homogeneously dispersed in ethanol solution by ultrasonic homogenizer. The stability of the suspension was measured by zeta sizer (Malvern NanoZS). Prepared TiO_2 based solutions were coated on glazed ceramic tiles with spray coating technique. The coated ceramics were heat treated at 950°C. Methylene blue aqueous solutions were prepared in 5mg/L, 15mg/L and 30mg/L concentrations by dissolving the dye in distilled water. All polluted tiles were placed under direct sunlight irradiation between 0 to 120min. Colorimetric measurements were evaluated using colorimeter (Minolta 3600-d) in order to determine photocatalytic performance of unmodified and Si modified tiles. Surface morphology of coated tiles and TiO_2 powders were characterized with scanning electron microscopy (SEM, Zeiss Supra 50VP, Zeiss Evo 50EP). X-ray diffraction method (XRD, Rikagu-Rint 2200) were used to obtain effect of the Si addition on composition and crystal stucture of the TiO_2 powders at above phase transition temperature.

3. RESULTS

Controlling the size of TiO_2 at nanometric scale for high temperature applications is important, because photocatalytic activity is more efficient with increasing surface area. Figure 1a shows the SEM image of TiO_2 powder, used in this research. The particle size is in the range of 25-30 nm. Also, SEM image of Si modified TiO_2 particles at 950°C is given Figure 1b. It points out that, Si modified particles has no grain growth after heat treatment, and its grain size is nearly 30nm.

Unmodified and Si modified particles were annealed for 1-5h at 950°C to investigate phase transition from anatase to rutile. Figure 2 shows X-ray diffraction pattern of TiO_2 nanoparticles before and after heat treatment. Unmodified particles have 80/20 anatase and rutile ratio before calcination. Whereas, anatase phase completely transforms to rutile at 950°C for 1h. On the other hand, heat treated Si modified TiO_2 powders shows similar X-ray diffraction pattern as unmodified particles. From the results, anatase to rutile ratio (75/25) of Si modified particles is very close to pure TiO_2 particles with increasing calcination time. It can be explained that SiO_2 layer formation takes place on TiO_2 surface or Si act as an interstitial dopant in the TiO_2 matrix due to its smaller ionic radious (Chen et al, 1999).

Figure 3a and Figure 3b demonstrate the surface morphology of spray deposited TiO_2 nanoparticles after coating and after sintering at 950°C for 1h. When the TiO_2 particles are coated with spray deposition technique, it can be seen that the TiO_2 particles are homogeneously distributed on tile surface (Figure 3a). After heat treatment, TiO_2 particles start to interact with glaze layer. It is observed in Figure 3b, some particles are embedded into the glaze surface after heat treatment. Movement of the particles into the glazed layer can be controlled with heat treatment and its duration. Because excessively embedded particles into the glaze layer will adversely affect photocatalytic performance of the tiles (Zan et al, 2004).

The degree of cleanability of the uncoated, unmodified TiO_2 coated and Si modified TiO_2 coated tiles were revealed by using 5-15-30mg/L methylene blue concentrations. Distilled water based methylene blue solutions were dropped on tile surface for pollution by automatic pipette. After pollution, all samples were placed under direct exposure to sunlight. Color values (L,a,b) of the tiles were recorded for before irradiation (initial state), after pollution (methylene blue polluted state) and after irradiation (final state). L,a,b results were compared in itself for each state. Percentage of the cleanability was calculated by : cleanability(%)=b_{tn}/b_{tin}*100 where b_{tn} is b value of at the end of a certain period of irradiation time after methylene blue pollution and b_{tin} is initial b value before methylene blue pollution. Figure 4 presents the results of the photocatalytic test.

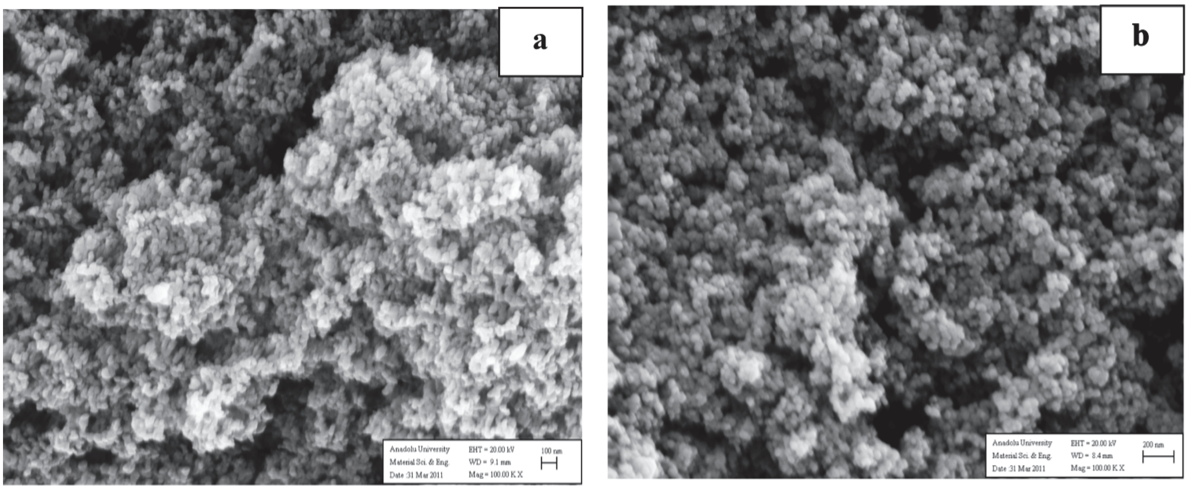

Figure 1. SEM images of unmodified TiO_2 (a) and Si modified TiO_2 particles (b)

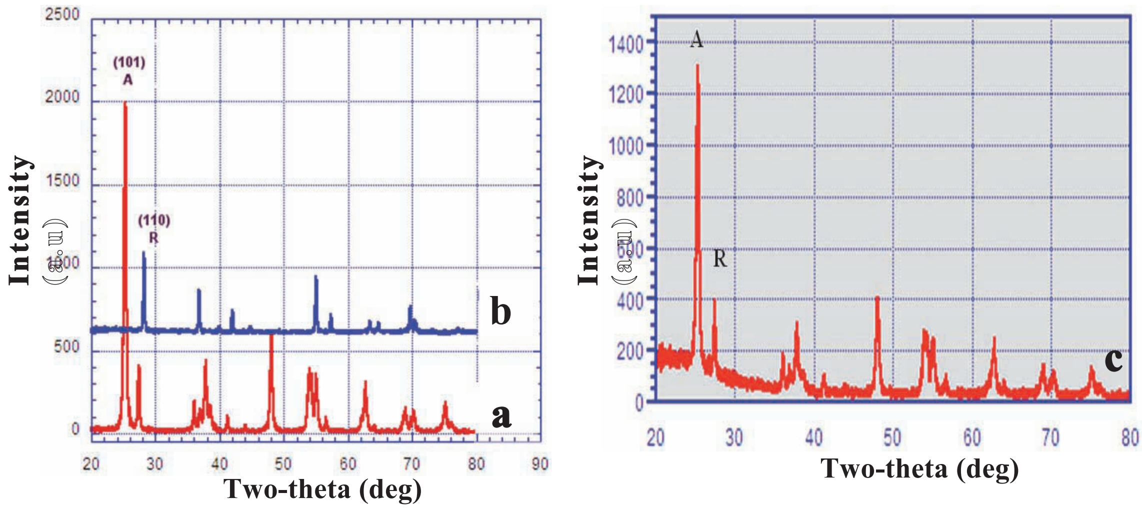

Figure 2. XRD patterns of unmodified (a), calcined and unmodified (b), calcined and Si modified TiO_2 particles (c)

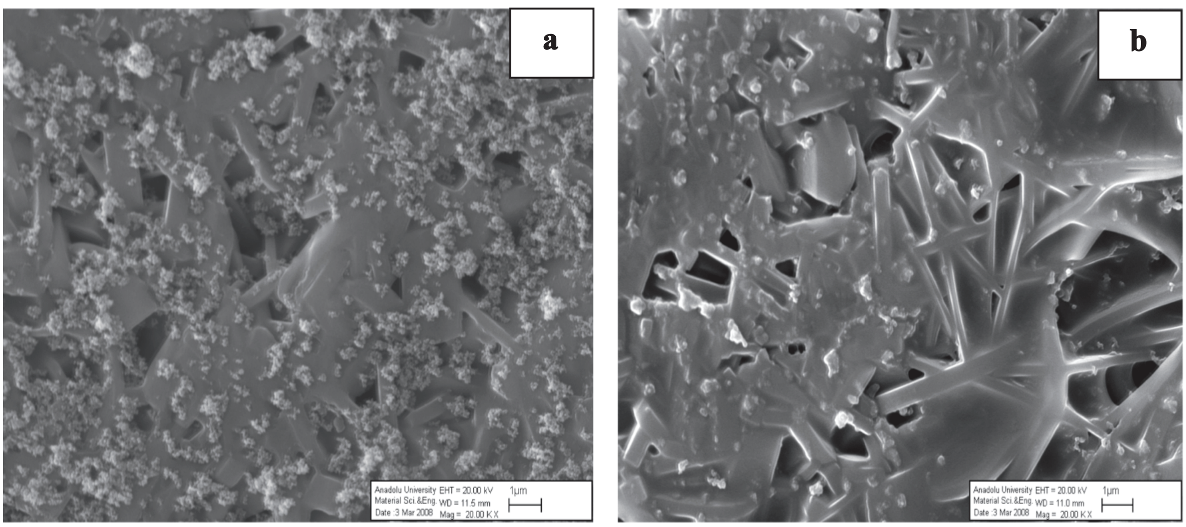

Figure 3. SEM images of TiO_2 coated tiles (a) after coating and (b) after heat treatment

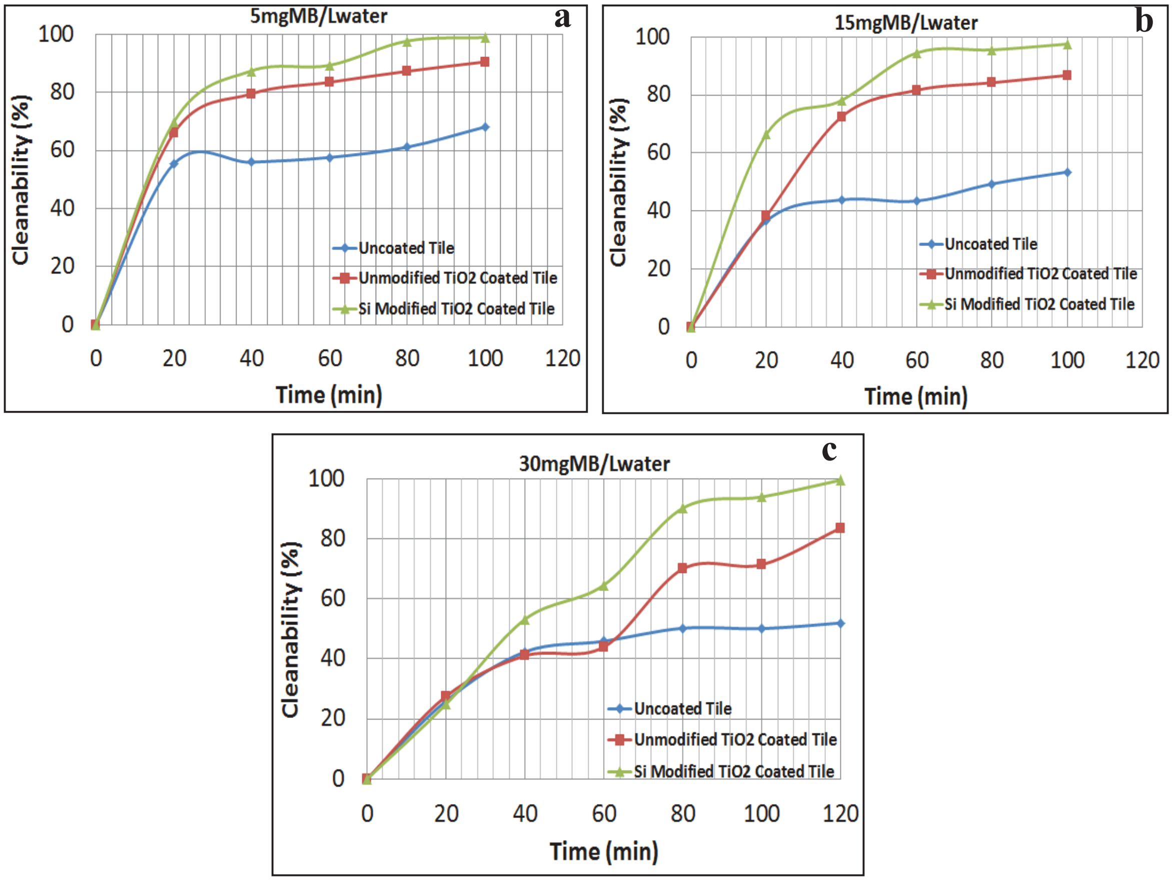

Figure 4. Photocatalytic performance of uncoated, unmodified TiO_2 coated and Si modified TiO_2 coated tiles for 5-15-30mg/L methylene blue concentrations

The degree of cleanability of the tile samples increases with irradiation time for all methylene blue concentrations as given Figure 4. The degree of cleanability of the uncoated tile and unmodified TiO_2 coated tiles are nearly 66% and 87% under irradiation for 100 minutes, respectively. On the other hand, when Si modified TiO_2 coated tiles are compared with unmodified TiO_2 coated tiles for same duration, it has a great improved photoactivity. Si modified TiO_2 coated tiles are cleaned completely after 80 minutes for 5mg/L methylene blue concentration (Figure 4a). As given Figure 4b, nearly all methylene blue are degraded after 100 minutes for Si modified TiO_2 coated tiles, whereas uncoated and unmodified TiO_2 coated tile has no perfectly photocatalytic degradation for 15mg/L. When concentration is increased to 30mg/L as shown Figure 4c, 52%, 84% and 100% of methylene blue are cleaned in 120 minutes for tiles. From the results, self-cleaning time of tiles increase with increasing concentration of organic pollutant. Also, photocatalytic ability of tiles can be enhanced by using Si modified TiO_2 particles.

4. CONCLUSION

TiO_2 nano particles were successfully modified using TEOS. Modified particles from XRD results showed that there were no phase transitions between anatase to rutile at 950^oC for 1-5h. Unmodified and Si modified particles were coated on glazed tile. The results pointed out that, completely degradation of methylene blue were observed using Si-modified TiO_2 coated tiles when compared uncoated and unmodified TiO_2 coated tiles. In conclusion, Si modified TiO_2 nano particles can be used both high temperature and low temperature applications such as ceramic, paint and textile due to its high photocatalytic ability and high thermal stability.

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