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Comparison of Ilmenite and Nano-Ilmenite for Dye Removal and Antibacterial Activities

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Abstract

Objective: There are différents méthode for moving dyes from contaminated environment and textile industries, the gold of this study is using of nano Ilmenite with anti bacterial properties for dye degradation.

Method: The Ilmenite nanoparticles were produced and their catalytic activities were determined by the color change of several dyes. The prepared $FeTiO_3$ nanoparticles have hexagonal structure with average size of ~21 nm.

Results: The results indicated that although the Ilmenite has catalytic activity for photo-oxidation of dyes but Nano-Ilmenite has higher activity for dye removal. Dye removal by Nano-Ilmenite for Malachite Green, Alkaline Fuchsin and Coomassie Blue were 97% 50% and 100% respectively. Ilmenite removed Alkalin Fusion in lower rate but increased the color of Malachite Green and Coomassie Blue. Although Ilmenite had antibacterial activity but antibacterial activity of Nano-Ilmenite was 50% more.

Conclusion: These data indicate that this Ilmenite soil can be used for remediation of contaminated area.

Keywords: Nanoparticle iron oxide; Photo-catalytic activity; Antimicrobial activity; Ilmenite; Dye; Degradation

Introduction

Dyes are among environmental pollutants, which released to the environment by pharmaceutical and textile industries, and are a major cause for some diseases. Dyes are mutagenic, toxic, and teratogenic, so they are a serious health threat to humans and other organisms. By releasing to the environments such as water, dyes are able to decrease or stop water reoxygenation through blocking sunlight and, as a result, to increase the BOD value that is a harmful condition for aquatic organisms. In green chemistry, dye removal from industrial wastewaters is one of the most important environmental concerns. Many Dyes are stable under hard conditions and are resistance to biodegradation, so to remove them from nature, effective and environmentally friendly materials are needed [1,2]. Photocatalytic degradation is a favorable, promising, clean, and green technology for the removal of dyes from water and wastewater. In such a process, a nontoxic semiconductor catalyst operates; so that while semiconductor is irradiated with light of a suitable wavelength, it becomes a powerful oxidant that converts most of the organic materials into carbon dioxide and water without producing any adverse by-products. Following by UV exposure, photosensitive semi-conductors generate active oxygen that oxidizes and disintegrates organic substances [3]. Since the role of sunlight in modifying organic compounds in the environment is recognized, therefore photo-oxidation reaction is based on the radiation wavelengths close to the sunlight. In the semiconductor-sensitized photo-oxidation process, metal semiconductors (TiO_2, ZnO, CdS, WO_3, and SnO_2) have been widely utilized in the photocatalytic processes for energy production and degradation of environmental contaminants via light-induced redox reactions [4]. Due to properties such as chemical stability, non-toxicity and high photocatalytic activity, the titanium dioxide powder was the most popular metal using in photocatalysis [5]. Nanotechnology has already a significant contribution to the advancement of technology in a number of industries. It generally refers to the fields of science and technology, and its general principle is to control the materials on the atomic and molecular scale (usually 100 nm or less). The development of nanotechnology has increased diversity in catalysts and photocatalysts. Ilmenite is an economically important mineral compound with the chemical formula $FeTiO_3$, which is one of the most important sources for titanium. It is an opaque mineral with a hexagonal structure that is black to brownish-red with a metallic or submetallic brightness. It is a semiconductor with a band gap of 2.58-2.9 eV, so has potential applications in chemical catalysts and photocatalysts [6,7]. Ilmenite is low-priced and can be found in different geographical locations [8]. Considering catalytic and antimicrobial properties of Ilmenite, in this study, Ilmenite were prepared as nanoparticle and then its catalytic and anti-microbial properties were studied.

Material and Methods

Dye removal

The photo-catalytic activities of the prepared Ilmenite Nanoparticles were evaluated by studying the degradation of Malachite Green with concentration 0.001 µg/ml, Alkaline Fuchsin with concentration 0.001 µg/ml, and Coomassie Blue with concentration 0.01 µg/ml, in present of Ilmenite nanoparticles, under the light and the dark conditions. The Catalytic properties of both Ilmenite and Nano-Ilmenite studied in 3 plates, each plate contained 10 µL of each dyes with different colors. Then 5 mL of distilled water were added to each plate, with 0.1 g of either Ilmenite or Ilmenite nanoparticles and one plate used as blank, without addition of catalytic Ilmenite. Then all three plates exposed to UV light by UV cross linker (Uvitec) for 30 minutes and the color changes were recorded at 465, 624, 540 nm for Comassie Blue, Malachite Green and Alkaline Fusion, respectively. Also the catalytic activity of Ilmenite was studied in darkness conditions. Dyes removal determined by the changes in the absorbance, using Milton Roy spectrophotometer 21D.

Antibacterial activities

Activated sludge sample (biological floc composed of bacteria and

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protozoa) was added to three 15 ml Falcon tube with nutrient broth. First tube had 0.1 g of Ilmenite particles and the second one had 0.1 g of Ilmenite nanoparticles, while the third one was used as blank, without addition of catalytic. Then, all three Falcon tubes incubated in the daylight for 2 days. The same experiments were similarly prepared except the tubes incubated at complete darkness.

Samples were used to determine antibacterial activity of Ilmenite and Nano-Ilmenite against mixed culture of sludge. Each experiment was repeated at least three times in the darkness and the daylight. The samples were dilute and the numbers of colonies after 24 hours on nutrient agar were detected. Also maximum growth were determined by the changes in the absorbance at 600nm, using Milton Roy spectrophotometer 21D.

Nano-Ilmenite production

There are several methods for the production of nanopowders. Particle size reduction include milling, grinding, jet milling and crushing are among conventional methods. There are several disadvantages to these methods; firstly they are not able to accomplish desired amount of particle size reduction, Secondly substances like explosives, pharmaceutical and chemical intermediates cannot be treated with these methods as they are temperature and pressure sensitive. The common rule for size reduction is that as particle size decreases, electrostatic and even molecular interactions increase, leading to particle agglomerations, which cannot be reduced any further in size. For this reason, most time the grinding process has to be carried out in a liquid medium (colloidal grinding), which disperses the particles as much as possible.

However in this study the Nano Ilmenite produced by milling for 20 min, it was stable and its property was compared with Ilmenite by Spm model DMBE and D8 Advance Germany XRD.

Removal of color from oil by ilmenite nanoparticles

To investigate the effect of Ilmenite nano particles on kerosene ، kerosene was exposure to nano Ilmenite for 21 days, then the color changes determined. Absorbance of kerosene was measured at 420 wavelength by Milton Roy spectrophotometer 21D. Also Gas chromatography analysis by Agilent 7890A on kerosene that had been exposed to bacteria and Nano-Ilmenite was done.

Results and Discussion

Photo catalytic activity of ilmenite and nano ilmenite

The Ilmenite used in this study was in micron size, which was confirmed by XRD as shown in Figure 1. For having more catalytic activities the particles were grinding by mill ball.

For Nano-grinding in a ball mill, the grinding jar and balls have to be made of a very abrasion-resistant material, such as zirconium oxide, to minimize contamination of the studied sample. Factors like choice of dispersion medium or size of grinding ball have a crucial influence on the success of the process. Generally, small ball diameters (smaller than three millimeters or 0.12 inches) and grinding times of several hours are beneficial for the production of Nano-particles as substantially more energy and a greater surface are required compared to dry grinding in the micron range. The universe black powder in 21 nm obtained by grinding the Ilmenite by Planetary ball mill Production of farapajuh naghshe jahan. The AFM and Microscopic pictures are shown in Figures 2 and 3. Hexagonal shapes with micro in size of Ilmenite are shown in Figure 2a. In Figure 2b the size of particles are nano however the hexagonal shape are shown in Figure 3 detected by AFM.

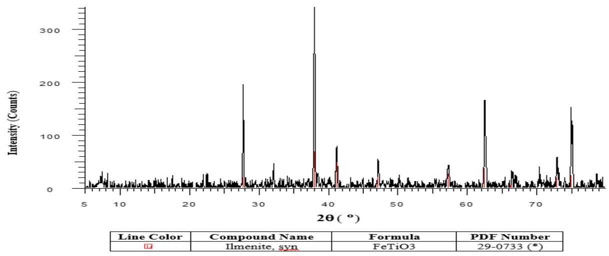

Figure 1: XRD pattern of Ilmenite by D8 Advance Germany XRD.

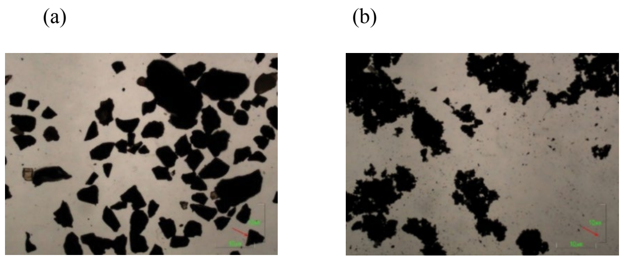

Figure 2: Microscopic pictures from fluorescent Microscope Nikon E200 (×100) of Ilmenite and nano Ilmenite (a) Ilmenite (b) nano Ilmenite.

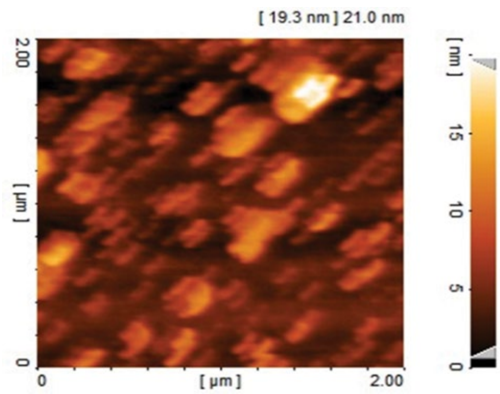

Figure 3: AFM picture of Nano Ilmenite by SPM model DMBE. The size of particles are 21 nm.

Ilmenite and Nano-Ilmenite both showed catalytic activity in the presence of dyes. These catalytic activities were different, depending on different dyes and different sizes of Ilmenite, while Nano-Ilmenite removed all dyes, showing higher catalytic activity than the Ilmenite. Regarding Alkaline Fuchsin, Nano-Ilmenite decreased 50% of color both in the dark and the light condition as seen in Figures 4 and 5.

While, in compare to Nano-Ilmenite, Ilmenite showed a very weak effect on dyes removal. Ilmenite increase the color of Malachite Green, while Nano-Ilmenite decrease the color 97% in the light and 75% in the dark as seen in Figures 6 and 7. The Ilmenite increased the color of Coomassie Blue in the light and removed this color in the dark, while Nano-Ilmenite showed 100% removal of this dye in both the light and the dark conditions as is evident from Figures 8 and 9.

Results indicate catalytic activity of Nano-Ilmenite and its role in dye removal. This property can be improved by UV light illumination and can be used in environmental protection. It has been reported that semiconductors (such as TiO_2, ZnO, Fe_2O_3,Cds, and ZnS) can act

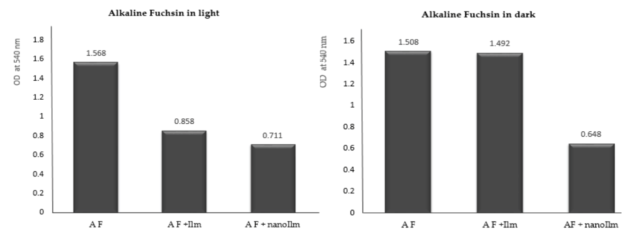

Figure 4: The above graph depicts the effect of Ilmenite and Nano-Ilmenite on Alkaline Fuchsin in dark and UV irradiation. The data are the mean of three experiments. As it has been shown the Nano-Ilmenite reduced the color more (AF=Alkaline Fuchsin) (AF+Ilm=Alkaline Fuchsin+Ilmenite) (AF+nanoIlm= Alkaline Fuchsin+nano Ilmenite).

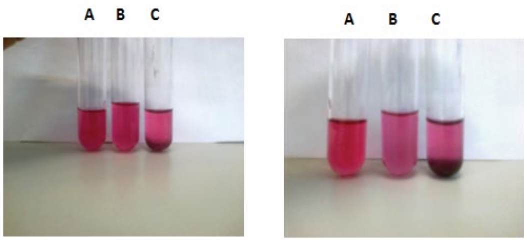

Figure 5: The effect of Ilmenite and Nano-Ilmenite on Alkaline Fuchsin in dark (up) and UV irradiation (down) (A)=Blank, (B)=dye with Ilmenite (C)=dye with nano Ilmenite.

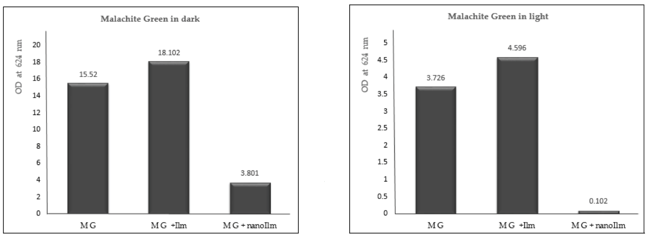

Figure 6: The above graph depicts the effect of Ilmenite and nano Ilmenite on Malachite Green in dark and UV irradiation. The data are the mean of three experiments. As it has been shown the Nano-Ilmenite reduced the color more (MG=Malachite Green) (MG+Ilm=Malachite Green+Ilmenite) (MG+nanoIlm=Malachite Green+nano Ilmenite).

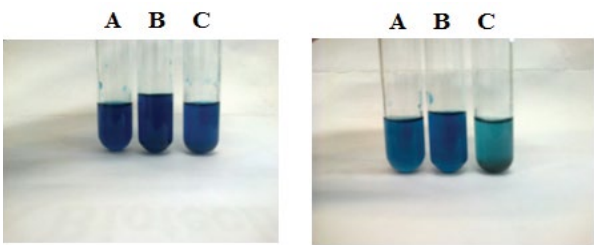

Figure 7: The effect of Ilmenite and nano Ilmenite on Malachite Green in dark (up) and UV irradiation (down)

(A)=Blank, (B)=dye with Ilmenite, (C)=dye with Nano-Ilmenite.

as sensitizers for light-induced redox-processes. ZnO was effective in the removal of Methylene Blue and Eosin Y and acid red 14 (AR14) from aqueous solution [9,10]. In recent years photochemical degradation has been done with TiO_2-catalyzed as a way to eliminate organic dyes from wastewater [3]. As the most approved material, it

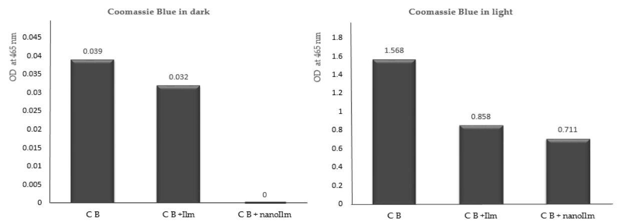

Figure 8: The above graph depicts the effect of Ilmenite and Nano-Ilmenite on Coomassie Blue in dark and UV irradiation the data are the mean of three experiments. As it has been shown the Nano-Ilmenite reduced the color more (CB= Coomassie Blue)/(CB+Ilm=Coomassie Blue+Ilmenite)/(CB+nanoIlm=CoomassieBlue+nano Ilmenite).

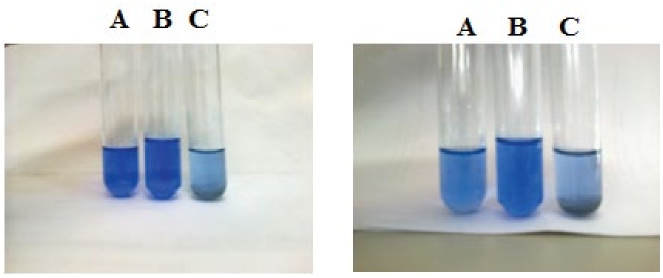

Figure 9: The effect of Ilmenite and nano Ilmenite on Coomassie Blue in the Dark (up) and UV irradiation (down)

(A)=Blank, (B)=dye with Ilmenite, (C)=dye with Nano-Ilmenite.

is a metal oxide semiconductor, which is very photoactive, although it does have a large band gap and only absorbs in the UV [3]. Titanium dioxide due to its properties such as being inexpensive, insoluble under most conditions, photochemically stable, and nontoxic, is used in Photocatalytic degradation of dyes; for example Chyuan and Chuan studied the process in photo-bleaching methyl orange that the dye were decolorized after 40 minutes of reaction [11-13]. In the presence of TiO_2, Photocatalytic oxidation of methylene blue, Rhodamine B, and methyl orange, was demonstrated by Matthews [14]. Coupled $FeTiO_3$/TiO_2 at a nanoscale demonstrated greatlt enhanced photocatalytic activity in removing 2-propanol in gas phase [15]. The thermo- and photo-catalytic activities of MnO_x/TiO_2 were used for the degradation of 2-naphthol, used as a model water pollutant [16]. The existence of TiO_2 strongly influence the photo-degradation of Safranin-T in the presence of UV light [5]. Fe_2O_3-TiO_2 composites showed high activity of photocatalytic degradation process [11]. Ilmenite is a composite of iron and titanium and its photocatalytic degradation is due to existence of TiO_2 in this mineral compound. Earths crust are full of this mineral and it is one of most important sources for production of titanium. Ilmenite is modified to titanium due to great applications of this such as solar cells, batteries and photocatalysts [17].

Anti-bacterial activities of nano-ilmenite and ilmenite

The counted colonies (number of colonies (CFU) of bacteria) showed that Nano-Ilmenite and Ilmenite have anti-bacterial effect. In addition, optical density of media detected at OD=600nm by spectrometer. The results showed that there is different in antibacterial activities of Ilmenite and Nano-Ilmenite. The anti-bacterial activities of nano Ilmenite was more than Ilmenite as shown in Table 1. Ilmenite nano particle and Ilmenite decrease the amount of bacteria 80% and 50 % respectively in darkness. The antimicrobial activities of these particles are more in darkness, however Nano-Ilmenite has more antimicrobial activities in visible light illumination and darkness compare to Ilmenite.

Surprisingly Ilmenite that we used had only some bacterial spore and the growth of some Bacillus strain have seen with incubation of unsterile Ilmenite on NA. These data indicated that this compound had anti-bacterial activities. We use activated sludge to detected antimicrobial activities, since Ilmenite was contaminated to Bacillus and autoclaving might change the structure of this component. The data was interesting and showed this soil reduces the optical absorption at 600nm and the bacterial count of activated sludge treated with Ilmenite reduce 60% compare to untreated one. Also the results showed that Ilmenite has more antibacterial activities when the activated sludge was treated with Ilmenite in day light compare to dark.

Titanium dioxide photocatalysts have many utilizations containing antiseptic, air and water sterilization, neutralize the odor, and pollution control. Titanium dioxide is a chemically stable material, and can continuously use antimicrobial effects Previous studies have investigated the antibacterial capabilities of visible light-responsive photocatalysts using the model bacteria *Escherichia coli* and human pathogens. The modified TiO_2 photocatalysts remarkably decreased the numbers of existence bacterial cells in response to visible light illumination. They also remarkably decreased the activity of bacterial endospores; decreasing their toxicity while maintaining their germinating abilities. TiO_2 photocatalysts are more useful than the traditional UV light-responsive TiO_2 photocatalysts because they do not require injurious UV light irradiation to operation. These photocatalysts, thus, provide a hopeful and beneficial way for disinfection of pathogenic bacteria; promote the prevention of infectious diseases [18,19]. Also in previous studies hydroxyapatite antibacterial powder modified with titanium oxide, was synthesized and it was established that have antibacterial and antifungal effect [20]. The bacteria could adsorb Fe^{3+} and reduce this metal. Iron had significant bacteriostatic effects, which were directly proportional to the iron concentration and the pH has effect on this event. Although Iron is a nutritionally essential trace element and has important functions in the metabolic, but iron is a devastating metal and reacts with H_2O_2 to form a hydroxyl radical HO which is known to be a highly reactive, indiscriminate oxidizing agent, which can damage proteins and nuclear acids. Thus, aerobic microorganism's growth will be prevented by iron too [21]. In present study the nano Ilmenite had the anti-bacterial activities more than Ilmenite (Ilmenite is a weakly magnetic titanium-iron oxide mineral) and the light promote anti-bacterial activities, we assume the anti-bacterial activities of Ilmenite is belong to Ti and Fe ion which are prepared in nano, therefore this is real promising to make reactors for water disinfection with Ilmenite to prevent water contamination or to make anti-bacterial ceramics.

Removal of color from oil by ilmenite nanoparticles

Result indicate that Nano-Ilmenite has been able to remove kerosene color. The results are shown in Table 2.

Nano-Ilmenite and bacteria have been able to reduce some of the compounds in kerosene. Table 3 shows some of these components. As it is shown, 87% of the color is removed, however the aromatic compound (pyrene) is removed only by 10.7%. However in industry the pyrrolidone are used for decolorization of petroleum oil which is carcinogenic substance [23].

OD at 600nm			
Experiment condition	**Nano Ilmenite+AS**	**Ilmenite+AS**	**AS**
At Light	0.487	0.798	0.810
At Darkness	0.195	0.515	0.930

Table 1: The Antibacterial activities of Ilmenite and Nano-Ilmenite on activated sludge (AS=Mixed bacteria in waste).

OD at 420 nm	
Kerosene exposure to Nano Ilmenite	**Kerosene**
0.18	0.242

Table 2: Nano-Ilmenite influence on reducing kerosene color.

Reduction%	Time exit the GC with FID Column	Probability name of substances
87	5	X
-	14.30	Naphthalene
-	15.50	M-naphthalene
-	21	Feluorene
-	25	Anthracene
6	27	X
3.75	28	Fluoranthene
10.7	30	Pyrene
11.5	32	X
11.5	33	X
7.7	35	Benzo anthracene

Table 3: Table prepared by the gas chromatography analysis by Agilent 7890A of kerosene that had been exposed to bacteria and Nano-Ilmenite.

Conclusions

In conclusion since Ilmenite is an economically important mineral and has potential in chemical catalysis, it is important to study the nano structure of this compound. These particles are cheap and can be convert to stable nanoparticles which are good candidate for remediation of aromatic and dyes from soil and water. The nanoparticle are promising catalytic mineral which can be used for removal of pesticide in agricultural soil or petroleum from contaminated soil. Ilmenite is heavy and can be removed from water by precipitation after useful proceeds. However nano Ilmenite is small and hard to remove therefore is better to use entrapped nano Ilmenite for their catalytic activities.

Results indicated that Nano-Ilmenite and bacteria have been able to reduce yellowish color of kerosene also some of the compounds in kerosene which were detected by GC.

Nano-Ilmenite is safe and inexpensive material that is able to decrease yellowish color of kerosene so in this research we approached to the nanoparticles which is cost-effective, sustainable and environment-friendly catalyst for dye removal and bacterial control.

Conflict of interest

There is no conflict of interest to author for this work.

Acknowledgment

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