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Low-cost Process for the Synthesis of Sorbents from Ilmenite Ores in Abu Ghalaga, Egypt, and their Uses in Biological Activity

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Abstract

Ilmenite ores have been extensively studied for biological activity, especially antibacterial and antifungal activities. Herein, we report a green approach to fabricating Fe-O/Ti-O composite from ilmenite ore. The composite was synthesized by a one-step reaction of ilmenite at 900°C in 2 h, the raw composite was, then, ground by a ball-milled process in 4 h to obtain the final produced composite. The obtained composite was characterized using a UV/Vis spectrophotometer, energy-dispersive X-ray spectrometry (EDX), and Fourier-transform infrared spectroscopy (FTIR). The weight percentages of the main elements in the ilmenite matrix was carbon (9.5%), oxygen (39.3%), titanium (15.1%), iron (24.0%), terbium (4.7%), molybdenum (2.6%), magnesium (1.8%), silicon (1.7%), and aluminium (1.3%). Several peaks were observed in the FTIR spectrum at 1086, 1009, 547, and 436 cm^{-1} which characterize the matrix of Ti-O and Fe-OAlso, the energy band gap was determined giving 3.52 eV. The produced composite was tested against different microbes using the agar well diffusion method and minimum inhibitory concentration (MIC) tests. It revealed good antimicrobial action against both Gram-positive (inhibition zone = 16 mm, MIC = 150 µg/ml) and Gram-negative bacteria (inhibition zone = 12 mm, MIC = 175 µg/ml) as well as fungi (Inhibition zone = 10 mm, MIC = 225 µg/ml). The obtained results are very promising for using the Ti-O/Fe-O composite as a strong antimicrobial agent in different industrial and pharmaceutical applications.

Keywords: Ilmenite, low-cost process, Ti-O, Fe-O, MIC, antibacterial, antifungal.

Introduction

Antibiotic-resistant bacteria have been known to exist virtually since the beginning of the antibiotic era, but over the past few decades, they have become more prominent. Others have suggested that a post-antibiotic era is soon to arrive because of the rapid growth of resistance and a reduced supply of antibiotics. Moreover, it is difficult to find a new useful antibiotic among the several toxins produced by these organisms, especially considering that the majority of frequently produced antibacterial molecules for these bacteria have certainly all already been identified (Fair and Tor, 2014).

Recently, metal oxides have emerged as promising candidates to challenge the rising global issue of antibacterial resistance because of their higher stability and selectivity when compared to organic antibacterial. Metal oxides such as Fe_3O_4, TiO_2, CuO, and ZnO are being carefully studied as new possible antibacterials (Stankic et al., 2016). They are appropriate for use as anti-bacterial agents in textiles (Dastjerdi and Montazer, 2010), skincare products (Nohynek et al., 2007), biomedical (Applerot et al., 2012), food-additive industries (Blecher et al., 2011), and water purification (Naseem and Durrani, 2021) because of their low toxicity towards human cells (Reddy et al., 2007), inexpensive (Huh and Kwon, 2011), size-dependent effective inhibition against a wide variety of bacteria, capability to avoid biofilm formation (Dastjerdi and Montazer, 2010; Kotrange et al., 2021), in addition to eradicating of spores (Stoimenov et al., 2003).

Ilmenite is a weakly magnetic mineral that has the chemical formula $FeTiO_3$. It is an iron-black, opaque mineral with a metallic or submetallic luster. Ilmenite is a hexagonal-structured mineral found in igneous rocks or black sands in many parts of the world (Anthony et al., 2001). According to the U.S. Geological Survey (2023), around 90% of the world's titanium mineral consumption is made up of ilmenite. Ilmenite has not been utilized extensively except for producing TiO_2 as a white pigment and creating new photocatalysts (Thambiliyagodage et al., 2021; Charitha et al., 2021). Therefore, giving more value to Ilmenite sand is a must.

Ilmenite has been studied as an antibacterial in many ways. For example, it has been examined as a degradation catalyst of lignin resulting in inhibiting bacteria with a range diameter zone of ±20 nm (Maulidiyah et al., 2019). Additionally, the nanocomposite g-$C_3N_4/Fe_2TiO_5/\alpha\text{-}Fe_2O_3$ gave an anti-bacterial activity of 32.8% against Gram-negative bacteria *Escherichia coli* (Thambiliyagodage et al., 2022). Moreover, Thambiliyagodage, Usgodaarachchi, et al. (2022) concluded that the growth of *E. coli* (69%) and *Staphylococcus aureus* (92%) was reduced by TiO_2-Fe_3C-Fe-Fe_3O_4/graphitic carbon composites under visible light. Likewise, Kalantari and Emtiazi (2016) reported that ilmenite soil can be used for the remediation of microbial contamination. This study aimed to provide a simple method for the synthesis of Fe-O/Ti-O composite from ilmenite ore. The characterizations and antimicrobial action of the composite were also investigated.

Materials and Methods

Preparation of ilmenite

Ilmenite ore was mined from the Abu Galaga deposit which occurs on a hill overlooking Wadi Abu Galaga, 20 Km west port of Abu Ghusun. The rocks were cut and then the non-oxidized inner part was ground to 0.074 mm by using a pulverizer. The powder is then treated by heating it at 900°C for 2 h. The raw composite was, then, grounded by a ball-milling process in 4 h to obtain the final produced composite.

Characterization of ilmenite

The optical properties of the ilmenite ore were studied using a UV/Vis spectrophotometer (Jasco UV/Vis Spectrometer v-630 (Jasco, Japan)). The electronic spectra of solid-state ilmenite ore were recorded in the range of 200–900 nm. Infrared (IR) spectra were carried out using a KBr disc (KBr pellet) on a JASCO FTIR-410 spectrometer in the 4000–400 cm^{-1} region. Energy-dispersive X-ray spectrometry (EDX) was used to determine the elemental composition of the ilmenite ore using EDX, model JEOL JSM-6510 LV, USA. EDX analyses were carried out at the Electron Microscope Unit, at Mansoura University.

Biological activity

Agar well diffusion method

The antimicrobial activity of the prepared composite was tested against Gram-positive bacteria (*Bacillus cereus* ATCC 10987) and Gram-negative bacteria (*Escherichia coli* ATCC 33456) and *Candida albicans* ATCC 10231 as a pathogenic fungus. The agar well diffusion method was performed according to the guidelines of the Clinical and Laboratory Standards Institute. Mueller-Hinton agar (MHA) medium was prepared and autoclaved. Then, the cool molten agar media were inoculated with 100 µl culture of each strain (0.5 McFarland standard (1-2×10^8 CFU/ml) and then poured into sterile Petri dishes in triplicates. After solidification, 200 µl of 500 µg/ml of the composite was prepared and added into the small wells (5 mm). Plates were incubated at 37°C for 48 h. After the incubation, zones of inhibition (ZOI) were measured in millimeters (mm).

Minimal inhibitory concentration (MIC)

Mueller-Hinton broth (MHB) was prepared, distributed into 100 ml conical flasks, and autoclaved, then inoculated with 100 µl of *B. cereus*, *E. coli*, and *C. albicans* (0.5 McFarland standard (1-2 × 10^8 CFU/ml)) in two sets of conical flasks containing different dosages (25-250 µg/ml) of the composite concentrations. The inoculated flasks were incubated at 100 rpm at 37°C for 24 h. The growth was measured spectrophotometrically at 600 nm against a negative control by measuring the optical density (OD) to determine the MIC value. Similarly, negative controls were made exclusive to the composite.

Statistical analysis

The data were statistically analyzed using SPSS version 18. All values in the experiments were expressed as the mean ± standard deviation (SD).

Results and Discussion

The ilmenite ore was extracted from the Abu Galaga deposit, which is located on a hill facing Wadi Abu Galaga, 20 km west of Abu Ghusun's port. The rocks were chopped, and the fresh ore was ground to 0.074 mm using a pulverizer. Energy-dispersive X-ray spectrometry (EDX) was used to determine the elemental composition of the ilmenite ore. The weight percentages of the main elements in the ilmenite matrix were carbon (9.5%), oxygen (39.3%), titanium (15.1%), iron (24.0%), terbium (4.7%), molybdenum (2.6%), magnesium (1.8%), silicon (1.7%), and aluminium (1.3%).
FTIR was used to identify the chemical structure and functional groups of an ilmenite ore sample. The FTIR spectrum of ilmenite (Figure 1) shows an absorption band at 3388 cm^{-1} which can be assigned to the stretching of -OH groups. The band at 2347 cm^{-1} was ascribed to the O=C=O stretching of carbon dioxide. The characteristic band located at 1598 cm^{-1} corresponds to the –OH bending. Several peaks were also observed at 1086, 1009, 547, and 436 cm^{-1} which characterize the matrix of Ti-O and Fe-O.
The spectra of ilmenite after heating to 900°C were shifted to the absorption band at 3438 cm^{-1} for -OH groups. Bands at 2347 and 1607 cm^{-1} were attributed to the O=C=O stretching and –OH bending. Several peaks were also observed at 094 and 478 cm^{-1} which characterize the matrix of Ti-O and Fe-O.

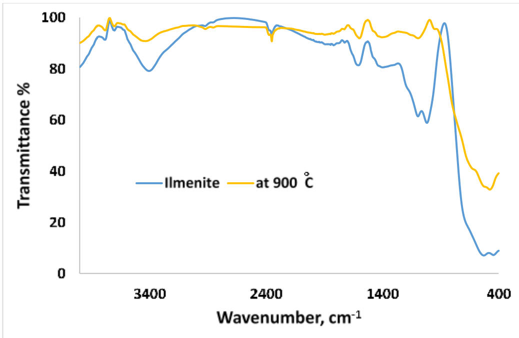

Figure 1: FTIR spectrum of ilmenite ore and the FeO-Ti-O composite.

The optical properties of the ilmenite ore were studied using a UV/Vis spectrophotometer. The diffuse reflectance spectra of solid-state ilmenite ore were recorded in the range of 200–900 nm (Figure 2) in water. They reveal that the ilmenite sample absorbs UV radiation very strongly at 234, 292, and 357 nm in a water medium. It has shown maximum peaks at 354 and 357 nm wavelengths with a reflectance of 0.3 and 1.2, which means that it exhibits good absorbance in the UV region.
Energy band gap of the material has been calculated by the following equation: $E = hc/\lambda$ where h is Planck's constant, c is the velocity of light ($hc \approx 1.24$ eV.µm) and λ is the wavelength of maximum absorbance. The band gap energy of the ore was measured by the above equation as 5.30, 4.25, and 3.47 eV at λ 234, 292, and 357 nm. This value indicates that the main content of ilmenite ore was titanium dioxide.
The ilmenite after being heated to 900°C was absorbed at 352 nm in a water medium. The band gap energy of these samples was 3.52 eV.

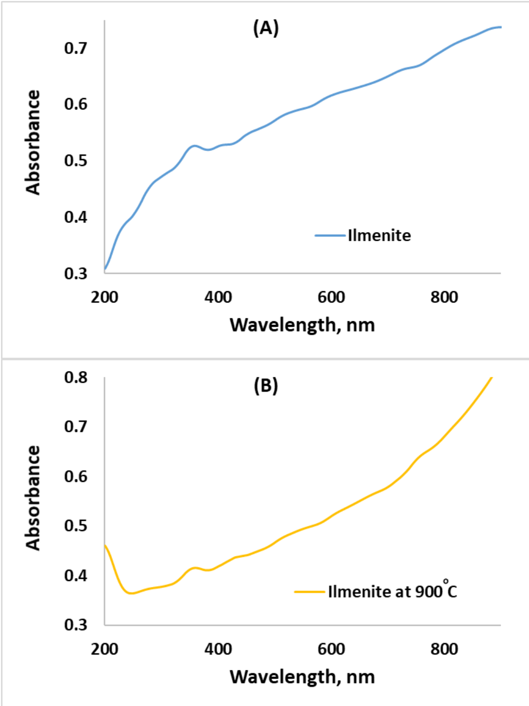

Figure 2. UV/Vis diffuse reflectance spectra of ilmenite ore in a water medium (A) and the prepared composite (B).

The band gap energy For the diffuse reflectance spectra was estimated by Tauc plot using the equation: $(F(R)h\upsilon)^{n} = \mathrm{C}\,(\,\mathrm{h}\upsilon\; - E_g)$ where $F(R)$ is Kubelka-Munk Function and $F(R) = \frac{k}{s} = \frac{(1-R)^2}{2R}$, where k is the Absorbence coefficient, s is the Scattering coefficient, R is the Reflectance, h is Plank's constant, υ Frequency, C Proportionality constant, E_g Band Gap energy, and n is nature of transmission equals $\frac{1}{2}$ for indirect allowed transition and 2 for direct allowed transition. by plotting E_g on x-axis versus $(F(R)h\upsilon)^2$ on the y-axis, The band gap was estimated from the intercept of the linear portion of Tauc plot on the x-axis (Figure 3).

The band gap energy of the ore was estimated using the Tauc plot and Kubelka-Munk Function as 5.25 eV. After being heated to 900°C, the band gap energy was estimated as 3.2 eV.

The obtained Figure 2. UV/Vis diffuse reflectance spectra of ilmenite ore in a water medium (A) and the prepared composite (B). composite showed a good antimicrobial effect with highly significant different values (P<0.05) between the tested microorganism and the diameter of the inhibition zone as shown in Table 1 and Figure 4. The concentrations of 500 µg/ml of FeO-Ti-O composite showed a biocidal action against both Gram-positive and Gram-negative bacteria as well as yeast. It produced an inhibition zone of 16 ± 0.06 mm against *B. cereus*, 12 ± 0.03 mm against *E. Coli*, and 10 ± 0.14 mm against *C. albicans*. An antibacterial activity test of ilmenite ($FeO.TiO_2$) against *E. coli*, *S. aureus*, *S. typhi*, and *X. oryzae* showed that each test had good activity in inhibiting bacteria with a range of the inhibiting diameter zone between ±20 nm as documented by Maulidiyah et al. (2019). Also, Ashraf et al. (2021) reported the bactericidal activity of silver phosphate-ilmenite nanocomposites supported on glycol chitosan mm against *S. aureus* and *E. coli* with inhibition zones of 13.60 ± 0.41, and 15.51 ± 0.52, respectively. The antimicrobial test showed 15 mg/g $FeTiO_3$ was active under visible light irradiation to inhibit *E. coli*, *S. aureus*, and *C. albicans* with diameter zones of 20.3 mm, 22.2 mm, and 22.7 mm, respectively, as reported by Watoni et al. (2017).

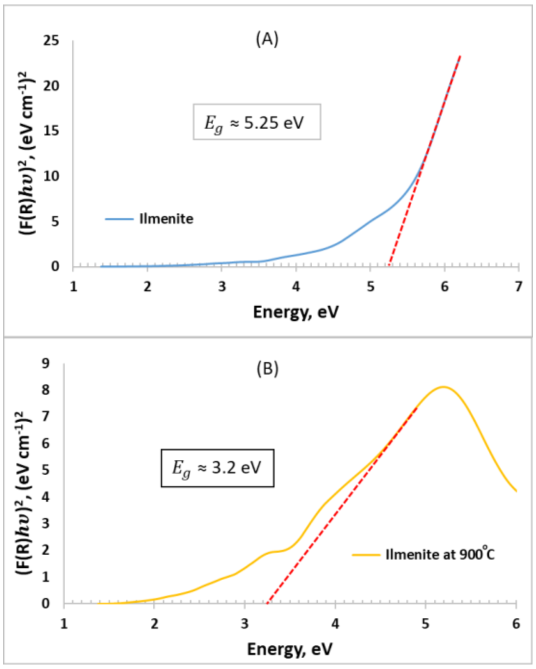

Figure 3. Tauc Plot of ilmenite ore (A) and the prepared composite (B).

Table 1. Agar well diffusion test of the prepared composite.

Microorganism	Zones of inhibition (mm ± SD)
Bacillus cereus	16 ± 0.06
Escherichia coli	12 ± 0.03
Candida albicans	10 ± 0.14

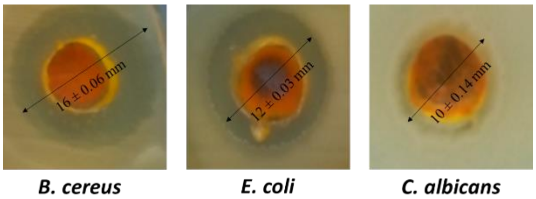

Figure 4. Antimicrobial activity of the prepared composite.

The antimicrobial action at 150 µg/ml showed a gradual inhibition action against *B. cereus*, *E. coli*, and *C. albicans*. More than 150 µg/ml, 175 µg/ml, and 225 µg/ml dosage against *B. cereus*, *E. coli*, and *C. albicans*, respectively, achieved 100% inhibition (MIC values) as shown in Figure 5. Therefore, the antimicrobial behavior of the composite showed a dose-dependent manner.

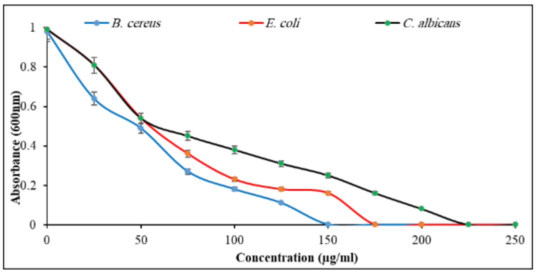

Figure 5. Minimum inhibitory concentration of the prepared composite.

Conclusion

Naturally modified Abu Ghalaga black ilmenite form was prepared by heating at 900°C for 2 h, characterized (UV/Vis spectrophotometer, energy-dispersive X-ray spectrometry (EDX), and Fourier-transform infrared spectroscopy (FTIR) and energy band gap) and tested for antimicrobial activity (agar well diffusion method and minimum inhibition concentration). With its low-cost and simple fabricating method as well as its fast and potent antimicrobial capacity, the Fe-O/Ti-O composite can be an excellent candidate for antibacterial and antifungal applications.

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الملخص العربي

عنوان البحث: تصنيع مواد ماصة منخفضة التكلفة من خامات الإلمنيت في أبو غلجا بمصر واستخداماتها في النشاط البيولوجي

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لقد احتلت دراسات النشاط البيولوجي لخامات الإلمنيت نطاقا واسعا من الاهتمام وخاصة الأنشطة المضادة للبكتيريا والفطريات. قدمت هذه الدراسة نهجا جديدا وآمنا لتصنيع متراكب أكسيد الحديدوز/أكسيد التيتانيوم من خام الإلمنيت. تم تصنيع المتراكب عن طريق تفاعل خطوة واحدة متمثلا في تسخين الإلمنيت عند ٩٠٠ درجة مئوية خلال ساعتين، ثم تم طحن المتراكب بعملية طحن استمرت ٤ ساعات للحصول على المتراكب النهائي. تم توصيف المتراكب الناتج باستخدام مقياس الطيف الضوئي للأشعة فوق

البنفسجية / المرئية، طيف الأشعة السينية المشتت للطاقة (EDX) والتحليل الطيفي للأشعة تحت الحمراء (FTIR). كانت النسب المئوية لوزن العناصر الرئيسية في الإلمنيت كالتالي: الكربون (٩,٥٪) ، الأكسجين (٣٩,٣٪) ، التيتانيوم (١٥,١٪) ، الحديد (٢٤,٠٪) ، التربيوم (٤,٧٪) ، الموليبدينوم (٢,٦٪) ، المغنيسيوم (١,٨٪).) والسيليكون (١,٧٪) والألمنيوم (١,٣٪). لوحظت عدة قمم في طيف FTIR عند ١٠٨٦ و ١٠٠٩ و ٥٤٧ و ٤٣٦ سم -١ والتي تميز وجود أكسيد الحديدوز وأكسيد التيتانيوم، تم تحديد فجوة نطاق الطاقة منتجة ٣,٥٢ فولت. تم اختبار المتراكب الناتج ضد الميكروبات المختلفة باستخدام طريقة انتشار الآجار واختبارات التركيز الأدنى للتثبيط (MIC). أظهر المتراكب تأثيرا جيدا مضادا للميكروبات ضد كل من البكتيريا الموجبة لصبغة جرام (بمنطقة تثبيط = ١٦ مم ،MIC = 150 ميكروجرام / مل) والبكتيريا السالبة لصبغة جرام (بمنطقة تثبيط = ١٢ مم ، MIC = 175 ميكروجرام / مل) وكذلك الفطريات بمنطقة تثبيط = ١٠ مم ، MIC = 225 ميكروجرام / مل. تعد النتائج التي تم الحصول عليها نتائج واعدة للغاية لاستخدام متراكب أكسيد الحديدوز/أكسيد التيتانيوم كعامل قوي مضادا للميكروبات في مختلف التطبيقات الصناعية والصيدلانية.