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Effect of Magnesium Oxide Nanoparticles (MgO) on Wastewater Treatment and Electric Current Generation Using Microbial Fuel Cell Technology

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Keywords:

Alternative Fuel; Renewable Energy; Bio-Electrical System; Generation Power.

Highlights:

- Nanotechnology provides new possibilities over conventional treatment techniques.
- More surface dependent properties due to high surface area to volume ratio.
- Nanomaterials as compared bulk materials show antibacterial activity.
- Best treatment due to their excellent adsorbent and valuable physicochemical properties.

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Abstract: The present study demonstrates the effect of MgO nanoparticles concentrations on industrial wastewater treatment and electricity generation by microbial fuel cells. The MgO nanoparticles were prepared chemically using reflux methods by mixing magnesium hydroxide with ethanol. X-ray diffraction (XRD), Scan Electron Microscopy (SEM), and Fourier Transform Infrared Spectroscopy (FTIR) were done for nanoparticle characterization. (Biological oxygen demand - BOD) and (Chemical oxygen demand - COD) were used as indicators to measure the acidity of wastewater. As a result, microbial fuel cells were proposed as a treatment method for wastewater. Nanoparticles with microbial fuel cell technology will always yield positive results in industrial water treatment. The results showed that using 0.025 mg/ml MgO nanoparticles in microbial fuel cells at pH 3 increased the COD degradation to (95.001%) through 30 min, BOD to (95.05%), and power voltage to (0.76) V. Therefore, treat the wastewater via microbial fuel cells were suggested. Nanoparticles with microbial fuel cell technology will always yield positive results in industrial water treatment.

تأثير أكسيد المغنيسيوم النانوي (MgO) على معالجة المياه الصرف الصحي وتوليد التيار الكهربائي باستخدام تكنولوجيا خلايا الوقود الميكروبية

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الخلاصة

الهدف من البحث إظهار تأثير أكسيد المغنيسيوم (MgO) النانوي على معالجة مياه الصرف الصحي وإنتاج التيار الكهربائي. تم تحضير أكسيد المغنيسيوم (MgO) النانوي كيميائياً باستخدام هيدروكسيد المغنيسيوم. وحددت خصائص الفيزيوكيميائية للمركب النانوي باستخدام مطياف الأشعة فوق البنفسجية (UV)، حيود الأشعة السينية (XRD)، المسح الضوئي المجهر الإلكتروني (SEM) والتحليل الطيفي للأشعة تحت الحمراء بتحويل فورييه (FTIR). وقد أظهرت النتائج أن جزيئات أكسيد المغنيسيوم (MgO) النانوي المحضرة كروية الشكل وبحجم 27,38 nm. تم دراسة تأثير استخدام أكسيد المغنيسيوم (MgO) النانوي عند الأس الهيدروجيني (pH) متغير على كل من معالجة مياه الصرف الصحي، نسبة الطلب على الأوكسجين الكيميائي (COD)، نسبة الطلب على الأوكسجين البيولوجي (BOD) وإنتاج التيار الكهربائي. أظهرت النتائج، أن استخدام أكسيد المغنيسيوم (MgO) النانوي بتركيز (0.025) ملي غرام/ ملي لتر عند الأس الهيدروجيني (3) كان الأكثر فعالية في معالجة مياه الصرف. حيث ازدادت نسبة COD إلى (95,001٪) خلال 30 دقيقة، وBOD إلى (95,005٪)، والجهد الكهربائي إلى (0,76) V. لذا تعد خلايا المايكروبية طريقة واعدة لمعالجة مياه الصرف الصحي. ان استخدام المركبات النانوية مع تقنية خلايا الوقود المايكروبي تأتي دائماً بنتائج إيجابية في معالجة المياه الصرف الصناعية.

الكلمات الدالة: الوقود البديل، الطاقة المتجددة، النظام الكهربائي الحيوي، توليد الطاقة.

1. INTRODUCTION

The importance of using biological processes in recovering energy from treating water and industrial wastewater can never be underestimated. Since the industrial sector has been producing high amounts of wastewater containing unhealthy organic substances, it is crucial to take the treatment seriously. It deserves to ensure that our environment is safe [1]. Even though untreated wastewater from industrial wastewater is allowed to accumulate, sometimes it causes the organic compounds to decay, which may release harmful gases in industrial wastewater treatment. The microbial fuel cells are rated attractive and useful ways to catalyze the electrical energy from carbohydrates and other organic matter in wastewater [2]. There are many advantages to applying microbial fuel cell technology in water and industrial wastewater treatment, such as producing little residue and being more stable during electricity production from wastewater treatment [3, 4]. Biological oxygen demand refers to oxidizing organic and nonorganic materials and decreasing the amount of dissolved oxygen by microorganisms in the wastewater. The higher levels of oxidizable materials in the wastewater refer to greater outcomes and biological oxygen demands [5]. Measuring the oxidation state in an aqueous solution is beneficial to notify the efficiency of biological conditions in degradation systems, like the relation between the nitrification rate and another biological process in an anaerobic state [6]. Nanoparticle focuses on studying nanoscale materials, opening a vast opportunity to comprehend physics and chemistry at the atomic level, which could aid in developing new materials that function effectively at such small sizes and regulate

various processes whose driving forces reside at the nanoscale; nanoparticles measured (1–100) nm are very effective as a reducing and reactive agent for various environmental purposes. The mixed reaction using nanoparticles comprises the following stages: (1) Surface mass transfer of nanoparticles from concentrated solution, (2) Surface adsorption of nanoparticles, (3) the chemical reaction on the nanoparticle, (4) the product adsorbing from the nanoparticles' surface, and (5) product movement to the bulk part of the solution [7, 8]. MgO is one of the most significant metal oxide nanoparticles because of multiple factors like nontoxicity and is easily prepared [9]. MgO nanoparticles have shown good behavior in adsorbing toxic agents [10]. They must distinguish chemical and physical characteristics like magnetic, electronic, optical, chemical, thermal, and mechanical properties [11]. The nanoparticles were differentiated using XRD, SEM, and FTIR. Meanwhile, a Multimeter was utilized to measure the voltage and current [12]. Recently, MFC technology exhibits the capability for wastewater treatment due to its numerous areas of interest [13]. However, it has not yet been used in the treatment of wastewater because of the disadvantages of this technology regarding low power production, high costs, and constraints in structure that must be overcome. Numerous outstanding investigations have already been published, addressing wastewater treatment via the MFC technology [14]. These studies investigated the most recent advancements in utilizing MFC in laboratories and industries, focusing on the integration of MFC with other processes in terms of practicability and effectiveness. Furthermore, these studies exhibited the

enhancement in the water treatment by using MFC technology compared to other technologies. Chen et al. [15] assembled a graphene sponge with three dimensions for use as an MFC anode. They demonstrated that the graphene sponge's microporous structure allowed the bacteria to grow well and achieve a higher MFC performance, leading to a higher power density than carbon felt. Yamashita and Yokoyama [16] utilized MFCs of molybdenum-based anode. Their results revealed a power density of $1296 \text{ mW}\cdot\text{m}^{-2}$ had been reached, although corrosion problems had been met over time. Additionally, the molecular diffusion and electron transport were enhanced, due to the active surface area that is provided by the dimensional properties of metal oxides, such as vertical 3D porous-based titanium oxide nano-sheets. However, a low rate of electron transfer and bacterial adhesion through bacterial respiration were reported while utilizing an anode made from metal oxide [17]. Nakamura et al. [18] suggested a new bacteria (*S. lochia* PV4) added with the nano- Fe_2O_3 colloids to MFCs to cross-link. Results exhibited increased productivity to 300% and enhanced long-distance electron transmission. Hu et al. [20]. A novel bicomponent composite of porous, self-assembling nanostructured $\text{Ni}_0.1\text{Mn}_0.9\text{O}_{1.45}$ was created as an anode electrocatalyst for increasing power output. The electrocatalyst had a porous nanostructure shaped like an ellipse. Each ellipse consisted of multi-nano-building blocks arranged on top of each other. This unique construction provides the capability to improve extracellular electron transfer from the anode to bacteria, in turn, increases a substantial area for bacterial colonization. Investigations into microbial fuel cells (MFCs) exhibited that a specially devised anode produced constant voltages exceeding 680 millivolts over prolonged periods, surpassing conventional carbon-felt anodes' performance in power generation. Previous investigations revealed that nanomaterials' geometric and structural properties significantly affect the efficiency of the extracellular electron transfer in MFCs. One study emphasized the application of $\text{Mn}_x\text{Cu}_{1-x}\text{Co}_2\text{O}_4$ spinel oxides, optimized by combining CoO_2 and MnO_2 with carbon substrates, used as cathodes in MFCs and created using an uncomplicated hydrothermal technique. These cathodes were evaluated compared to the traditional platinum (Pt) cathodes, in terms of their chemical oxygen demand (COD) reduction capabilities and power output density. The findings indicated that cathodes augmented with $\text{Mn}_x\text{Cu}_{1-x}\text{Co}_2\text{O}_4$ exhibited a superior power density of about $570 \text{ mW}\cdot\text{m}^{-2}$, outperforming Pt cathodes by roughly 87%. Moreover, these cathodes managed to decrease approximately 56% of the COD within nearly

240 hours of MFC operation [21,22]. In a distinct study, Yang and associates designed a microbial energy cell employing nitrogen-doped carbon aerogels, created by a temperature-regulated pyrolysis method from polyacrylonitrile. This innovative MFC showed a power output of $52.4 \text{ mW}\cdot\text{g}^{-1}$ and reached a peak power density of $1048 \pm 47 \text{ mW}\cdot\text{m}^{-2}$. This highlights the potential of the MFC technique for wastewater treatment due to its various beneficial aspects. Its practical use in wastewater treatment has not been achieved yet. Challenges such as low power output, expensive capital expenditures, and limited structural constraints need to be addressed. Several excellent research has been published on the applicability of MFC technology in wastewater treatment [14]. They talked about the latest advancements in Microbial Fuel Cell (MFC) technology in laboratory and industrial settings, focusing on the integration of MFC with other processes, their feasibility and efficiency, and comparing the quality of treated water with other technologies. Chen et al. [15] utilized an anode of 3D graphene sponge in MFC. A greater power density was achieved using a graphene sponge compared to carbon felt, likely due to the graphene sponge's microporous nature facilitating better bacteria growth and resulting in improved MFC performance. Yamashita and Yokoyama [16] achieved a power density of $1296 \text{ mW}\cdot\text{m}^{-2}$ in an MFC by utilizing a molybdenum-based anode, but encountered corrosion problems during extended operation. Moreover, the dimensional characteristics of metal oxides, like vertical 3D porous titanium oxide nano-sheets, enhanced the active surface area, facilitating electron transport and molecule diffusion. Metal oxides employed as anodes demonstrated reduced bacterial adherence and facilitated electron transfer via bacterial respiration [17]. Nakamura et al. [18] found that the addition of nano- Fe_2O_3 colloids to MFCs induced *S. lochia* PV4 bacteria to cross-link, creating a network topology that facilitated long-distance electron transmission and increased productivity by 300%. Hu et al. [20] created a new two-part composite material consisting of porous self-assembled nanostructured $\text{Ni}_0.1\text{Mn}_0.9\text{O}_{1.45}$ to serve as an anode electrocatalyst for enhancing power production. The electrocatalyst featured a porous nanostructure in an ellipsoidal shape, composed of several stacked nano-building pieces. The specific design offered a substantial surface area for the proliferation of bacteria and demonstrated exceptional electrocatalytic activity by promoting the exchange of electrons outside the bacterium, thus facilitating electron transfer between the anode and the bacterium. The anode created in the microbial fuel cell (MFC) continuously generated a voltage surpassing 680 millivolts for a prolonged

duration, but the carbon-felt anode yielded only a negligible quantity of energy. The impact of nanomaterial shape on the pace of extracellular electron transport has been convincingly proven [19]. A combined anode, consisting of reduced graphene oxide (RGO) and coated with nanoparticles of SnO₂ was used in a MFC by Mehdinia et al [24]. Results exhibited a significant increase in the power density by five times compared to an anode of only RGO. Findings attributed to the high conductivity and the large surface area of the combined anode that in turn enhanced the growth of bacterial biofilm and improved the electron transport. Additionally, the study explored the use of MnxCu_{1-x}Co₂O₄ spinel oxides, created through a direct hydrothermal method, as a novel component for cathodes. These were combined with carbon materials and tested against traditional Pt cathodes. Results showed that the MnxCu_{1-x}Co₂O₄-based cathodes increased power output density to about 570 mW.m⁻², marking an 87% improvement over Pt cathodes, and reduced the Chemical Oxygen Demand (COD) by 56% after around 240 hours of operation. In a separate study, Yang et al. constructed a microbial fuel cell using nitrogen-doped carbon aerogels, derived from pyrolyzed polyacrylonitrile, achieving peak power densities of 1048 ± 47 mW.m⁻¹ and a mass-specific power of 52.4 mW.g⁻¹. The main objective of this study is to prepare MgO nanoparticles and study their effect on degrading organic and inorganic compounds using Microbial fuel technology and nanoparticles to improve power generation and wastewater treatment, proving eco-friendly with renewable sources for generating electrical energy.

2.METHODS AND MATERIALS

2.1.Construction of Microbial Fuel Cell (MFC)

Two-chamber microbial continuous cathode fuel cell in which nanoparticles were used in the positive chamber for aeration, while the passive chamber was put in place to give a clear picture of wastewater treatment results in conjunction with the electricity production, which was put in place for sterilization bottles in the same experiment; each chamber was 30 mm diameter and a capacity of 100 ml. Two openings of 5.5 mm diameter were drilled in each cap to insert the salt bridge and electrodes, and 100 mL of potassium permanganate solution, 0.1 ml, was put into use. The container covers were sealed with adhesive tape. A Salt bridge was made with potassium chloride and agar in a 5 mm diameter tube. Graphite sheets with 0.2 mm thickness, a length of 50 mm, and a width of 12.5 mm as electrodes. Electrodes were submerged in one hundred percent ethanol for thirty minutes. Next, electrodes were treated with one mole of hydrochloric

acid, then one sodium hydroxide for one hour, and finally stored in distilled water before use. Copper wires were used to connect the electrode conductors; the multimeter was suspended to a 10-ohm resistor was used to complete the circuits. NITYDT-830D multimeter measured the voltage and current in the experiment. The investigations were conducted at room temperature between (20 to 25)°C and (30-50) % humidity rate [12]. The changes in wastewater sample pH were done using 1 N (HCl) and 1 N (NaOH) chamber microbial fuel presented in Fig. 1.

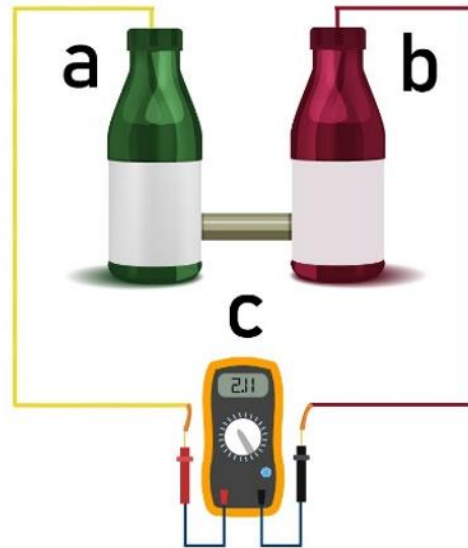
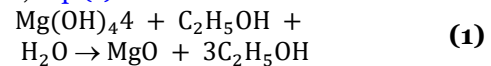


Fig. 1 Chamber Microbial Fuel Cell.

2.2.Preparation of MgO Nanoparticles

MgO nanoparticles are prepared using reflux by dissolving 5.72 grams of magnesium hydroxide in a solution consisting of 4.5 ml of distilled water in 50 ml ethanol. 0.6 ml hydrochloric acid was added, and homogeneous stirring was done to maintain the solution till the end of the reaction. MgO nanoparticles were dried for one hour at 100°C then calcined in the oven at 900°C for 13 hrs. MgO nanoparticles were optimized [9]. The chemical reaction is listed below, Eq. (1):



2.3.Biological Oxygen Demand and Chemical Oxygen Demand Analysis

Chemical oxygen demand analysis was performed using the open reflux method. The % COD remaining and standard error have been calculated using Eqs. (2) and (3) [25, 26], respectively:

$$\% \text{ COD remaining} = 100 - \left(\frac{\text{initialCOD} - \text{finalCOD}}{\text{initialCOD}} \times 100 \right) \quad (2)$$

$$\text{Standard error} = \frac{\text{Standard Deviation } (\delta)}{\sqrt{3}} \quad (3)$$

where; $\delta =$

$$\sqrt{\left(\frac{1}{N}\right) * \sum_{i=1}^N [(Xi - \mu)^2]} \quad (4)$$

The BOD analysis was performed using Young's [10] procedure with five days of incubation.

2.4. Analytical Methods

The microbial fuel cell's output voltage (U) was operated for a long period and computerized recording. The results used to find the density of power according to Eq. (5):

$$P = U \times j \quad (5)$$

where (j) is the current density ($A \ m^{-2}$), which is calculated by Eq. (6):

$$j = \frac{U}{R \times A} \quad (6)$$

Based on external resistance R (Ω) and the projected surface area of the cathode, Eq. (7) was used.

$$\text{Total Surface area} = 2 [(L \times B) + (L \times T) + (B \times T)] \times A \quad (7)$$

3. RESULTS

3.1. Characterization of Nanoparticles

The change of solution color to a white precipitate indicated the forming of the MgO nanoparticles. The results were confirmed through many tests, which included UV visible spectrum that showed a broadened beak at 450 nm, as shown in Fig. 2. The outcomes of (XRD) are presented in Fig. 3. SEM in Fig. 4 notifies the spherical shape and 27.38 nm size of MgO nanoparticles. The results of FTIR, which was measured by the equation of Scherrer in Fig. 5, confirm that common absorption bands listed in Table 1 formed the MgO nanoparticles. These results agreed with noticing that the hydroxyl group actively reduced metal ions [11].

Table 1 FT-IR Groupe Functions.

Peak with Maximum	Assigned
3429.2 cm^{-1}	OH stretch of water
1439.4 cm^{-1}	H ₂ O bending
above 3600 cm^{-1}	three -OH groups
above 1000 cm^{-1}	alkoxy group

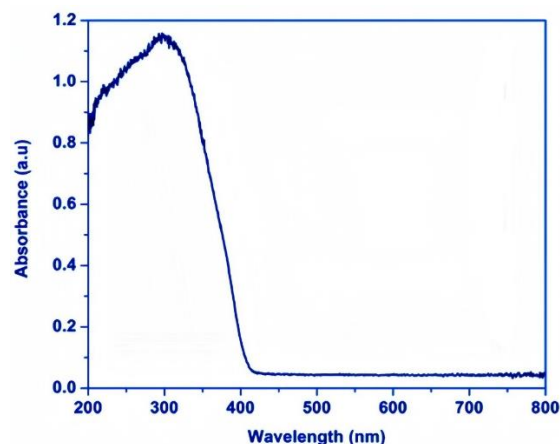


Fig. 2 UV-vis Spectrum for MgO Nanoparticles.

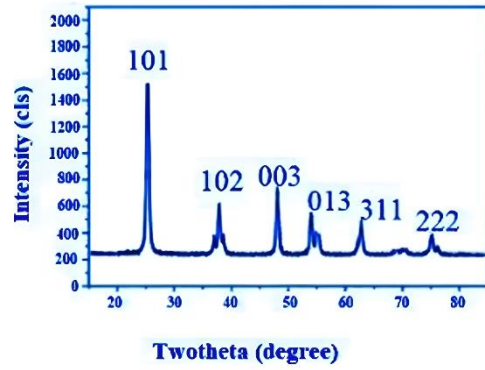


Fig. 3 X-ray Diffraction Analysis of MgO Samples.

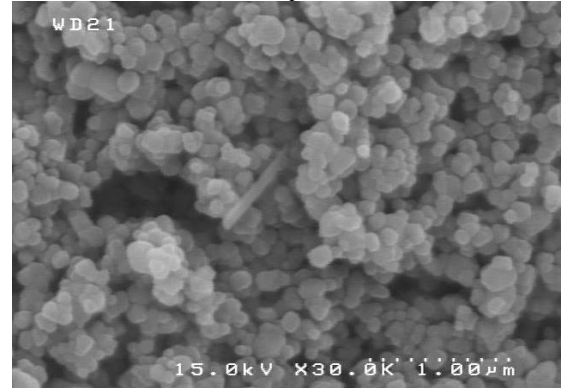


Fig. 4 SEM Images of MgO Nanoparticles.

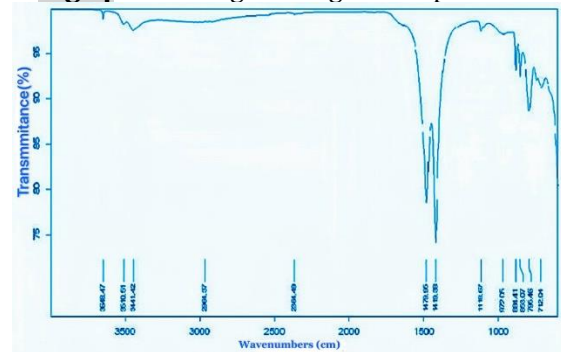


Fig. 5 FTIR Spectrum of MgO Nanoparticles.

3.2. Voltage and Current Measurements

MFC (Cell 1), which constructed from the aerobic sludge, was linked to a constant source of 10 Ω and periodically monitored to follow up the cell's outputs (voltage and current) to calculate the power and current densities both at a time. In previous studies, the highest current level in a normal double-chamber MFC had been observed at (7) pH [27]. This difference could be attributed to the impact of the chemical material that added to the wastewater. Nonetheless, in the present study utilizing MgO nanoparticles, the current was raised at pH 3 [14], and the current and power densities additionally showed 0.76 v.

4. DISCUSSION

The microbial fuel cell is a very important wastewater treatment method to generate electric power due to its ability to use a greater portion of the energy produced during the degradation of organic substances in

wastewater being used for electricity. However, when used as a wastewater treatment method, the microbial fuel cells produce less sludge than the conventional aerobic method [28]. Due to this benefit, Kim et al. [29] proposed the MFC as a wastewater treatment method.

4.1. Effect MgO Nanoparticles

Wastewater treatment by microbial fuel cells is a more affordable technology for developing nations worldwide because it combines wastewater treatment and electricity generation. Moreover, microbial fuel technology with MgO nanoparticles is the simplest and most eco-friendly technique that can meet the requirements of developing nations in the current state of affairs [27]. Scherer's Eq. (1) has been used to calculate the nanoparticle that produced via a liquid-phases reduction method. The rate size of the crystallite nanoparticle ranged between 35.6 nm to 24 nm after annealing the sample at 300°C for 3hr. SEM analysis indicates that the particles are spherical. Both systems showed their substrate removal potential, indicating the function of selectively enriched mixed bacteria in carbon source metabolism as electron donors. The removal efficiency of the substrate is relatively higher than the substrate. The degradation rate was documented using a

cathode with 0.025 mg/ml MgO nanoparticles at pH 3. During the stable operation phase, COD removal efficiencies of 95.001% in 30 min were noted, and 95.05% BOD was represented in Figs. (6-8).

4.2. Effect Wastewater pH

The impact of pH solution has been investigated using five levels of pH (3, 5, 7, and 7) and wastewater with 0.025 mg/ml MgO nanoparticles, which indicated that the climax in initial climate decomposition was found to be pH 3, showing the desired results for power output. In addition, pH 3 indicated the desired reduction in BOD and COD, confirming better wastewater treatment efficiency percentage and greater current and power densities [17, 18]. Therefore, a greater portion of the energy stored by the organic to toxic organic in the wastewater is turned into electric energy. Also, voltage and current, i.e., $A=V/R$, were recorded at regular phases and plotted for each pH. The power density was 0.76 v powers produced. More than a 50% reduction was observed. Figs. (9-12) and Table 2 exhibit that the microbial fuel cell has a significantly lower production additional sludge compared to the stander aerobic when utilized in the wastewater treatment [30, 31].

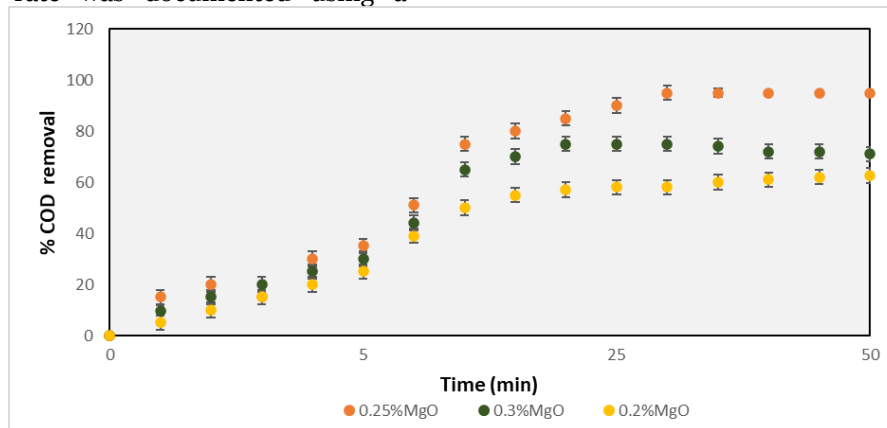


Fig. 6 MgO Concentration on %COD Removal at pH 3.

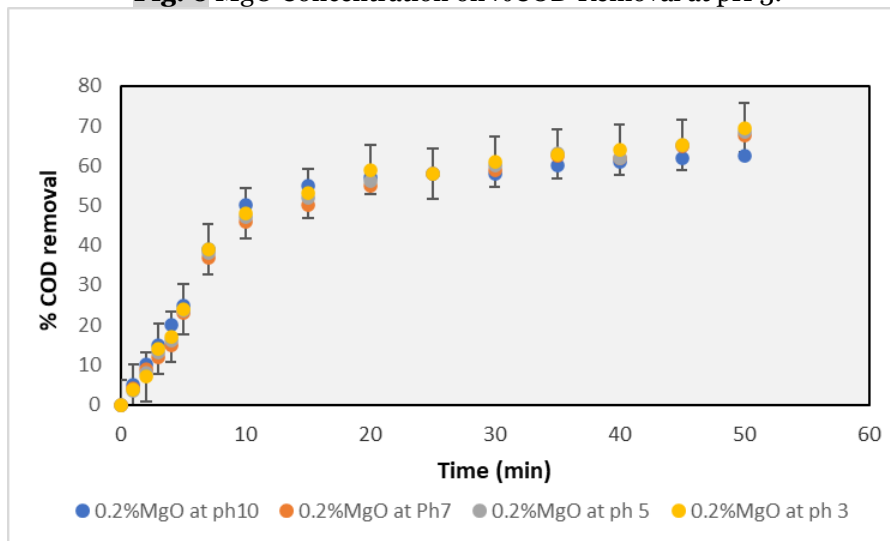


Fig. 7 0.2% MgO Concentration on %COD Removal at pH 3, 5, 7, and 10.

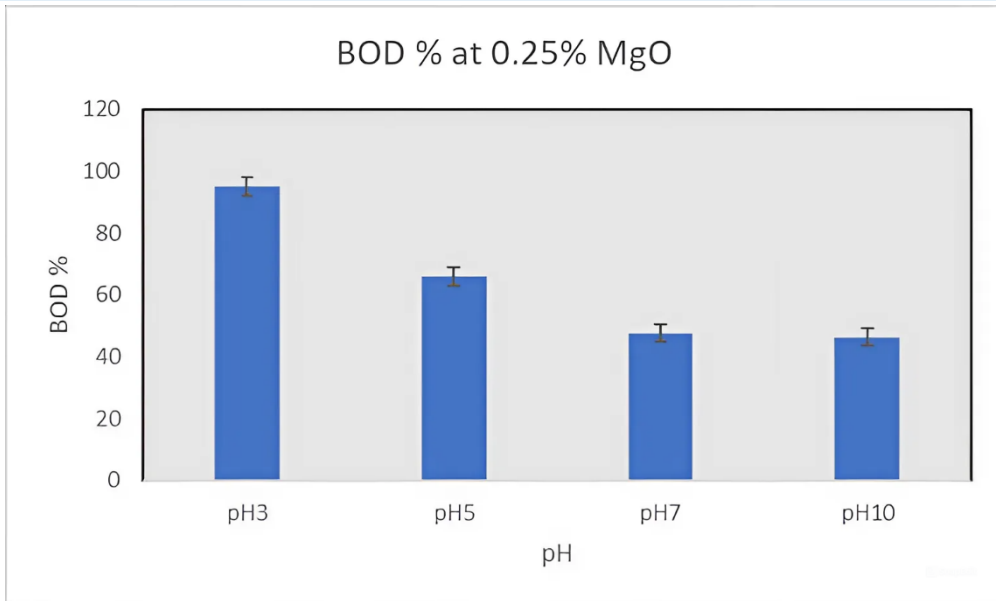


Fig. 8 0.2% MgO Concentration on %BOD at pH 3, 5, 7, and 10.

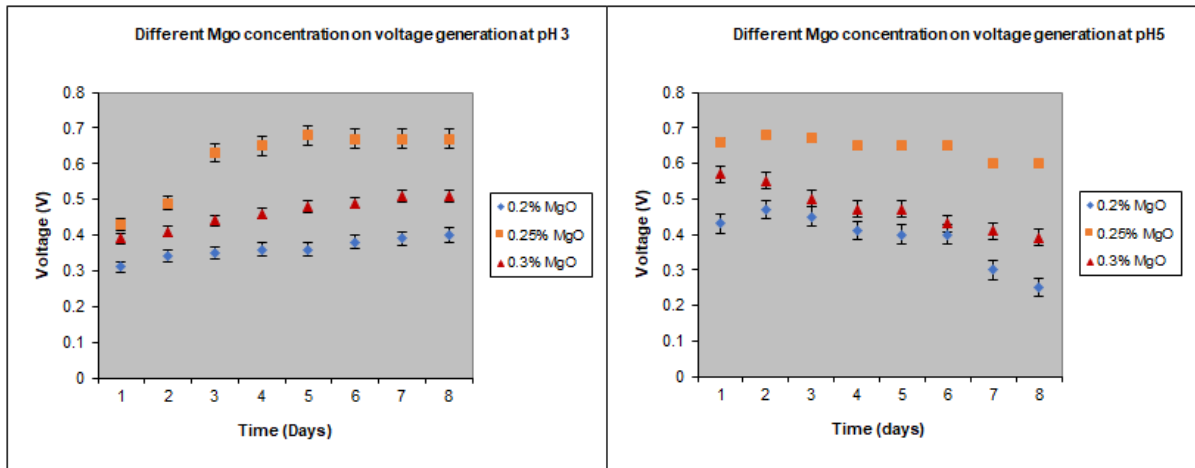


Fig. 9 MgO at pH 3 and 5.

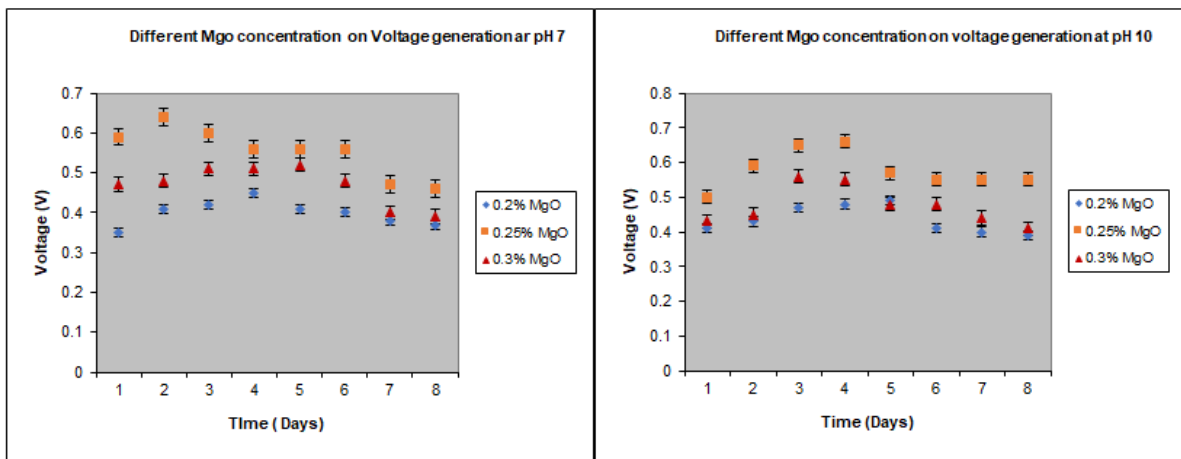


Fig. 10 MgO on Voltage Generation at pH 7 and 10.

Comparison of voltage for sample at PH 3,5,7,and 10 of 0.25%MgO

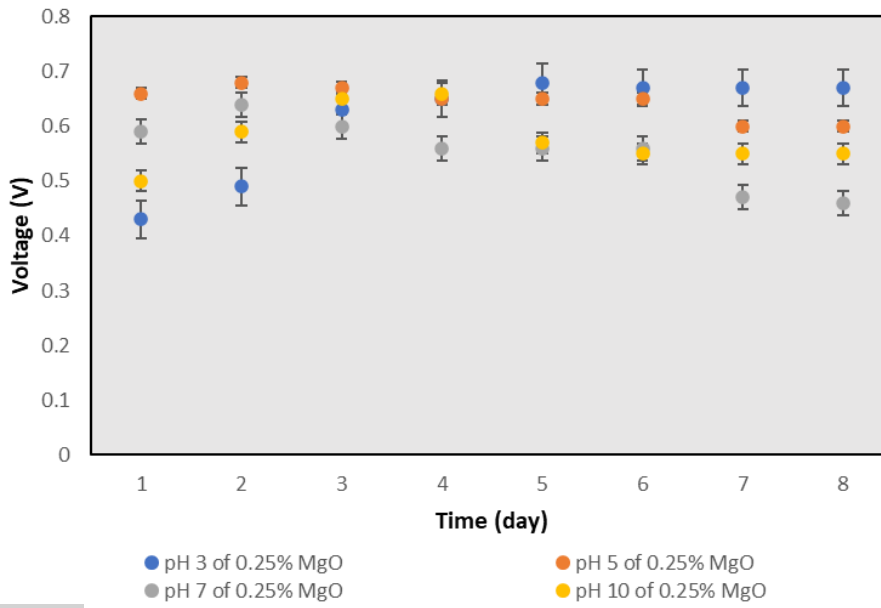


Fig. 11 0.25% MgO Concentration on Voltage Generation at pH 3, 5, 7, and 10.

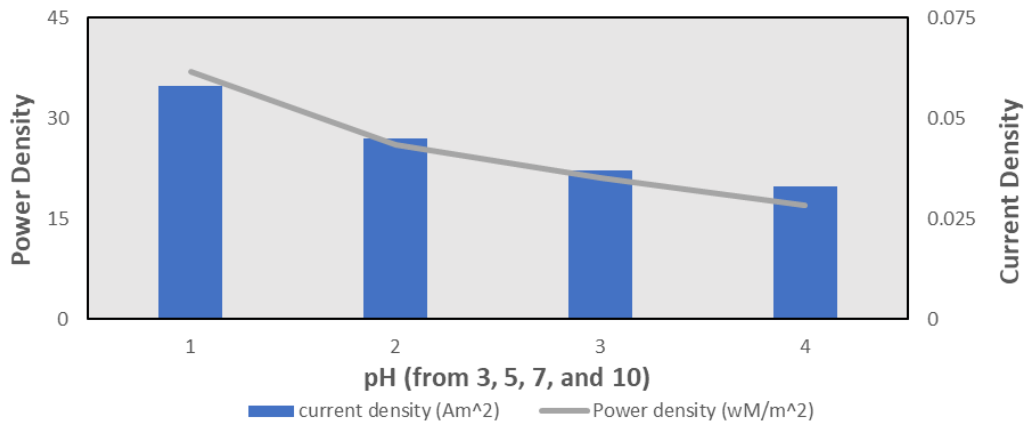


Fig. 12 Current Density and Power Density Produced by 0.25% MgO Concentration at pH 3, 5, 7, and 10.

Table 2 Comparison of BOD for Sample at pH=3 and MgO.

Ph3 and Con 0.025% MgO	Ph5 and Con 0.25% MgO	Ph7 and Con 0.25% MgO	Ph10 and Con 0.25% MgO
0	0	0	0
19.99	6.25	2.31	1.85
58.75	49.39	25.93	20.67
95.05	65.93	47.71	46.39

5.CONCLUSION

The present study found that wastewater can be used to generate electricity, which presents a new opportunity of renewable energy sources from wastewater treatment, hence, it's a promising and doable technology to generate electricity for developing and developed nations. The technology of combining wastewater treatment with electricity generation is affordable and eco-friendly, making it a potential solution to fulfill the needs of developing nations in the present scenario.

NOMENCLATURE

COD	Chemical Oxygen Demand.
BOD	Biological Oxygen Demand.
XRD	X-ray Diffraction.
SEM	Scanning Electron Microscopy.
FTIER	Transform Infrared Spectroscopy.
δ	Standard Deviation.
j	Current Density.
R	Resistance.
U	Voltage.
p	Power Density.
W	Watt.
B	Breath.
L	Length.
T	Width.
A	Ampere.
Ω	Ohm.

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