Effect of Ferric Oxide on Electricity Generation and Waste Water Treatment Using Microbial Fuel Cell Technology

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ABSTRACT

The aim of research is to show the effect of Ferric Oxide (Fe_2O_3) on the electricity production and wastewater treatment, since 2.5% of Ferric Oxide (Fe_2O_3) (heated and non heated) nanoparticles has been used. Characterization of nanoparticles was done using X-ray Diffraction (XRD) and Scan Electron Microscopy (SEM). The influence of acidity was also studied on both wastewater treatment on the Chemical Oxygen demand (COD) and Biological Oxygen Demand (BOD) and voltage output was studied. From the results, it was infused that the dosage of 0.025 g/l and an initial pH 7 were founded to be optimum for the effective degradation of effluents. The results concluded that the treatment of anaerobic sludge wastewater using Ferric Oxide (Fe_2O_3) in combination with microbial fuel cell technology is an efficient method for the treatment of anaerobic sludge wastewater.

Key words: Microbial fuel cell, nanoparticles, wastewater treatment.

تأثير أوكسيد الحديديك (Fe_2O_3) في توليد الكهرباء ومعالجة المياه باستخدام تكنولوجيا خلايا الوقود الميكروبية.

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الخلاصة

الهدف من البحث هو إظهار تأثير أكسيد الحديديك (Fe_2O_3) على إنتاج الكهرباء ومعالجة مياه الصرف الصحي، 2.5٪ من أكسيد الحديديك (Fe2O3) وقد استخدم (مسخن وغير مسخن) النانوية. وقد تم تحديد خصائص المركبات النانوية باستخدام حيود الأشعة السينية (XRD) والمسح الضوئي المجهر الإلكتروني (SEM).تمت دراسة تأثير الحامضية أيضا على حد سواء معالجة مياه الصرف الصحي على نسبة الطلب على الاوكسجين الكيمياوي (COD) ونسبة الطلب على الأوكسجين البيولوجي (BOD) وانتاج التيار الكهربائي تم دراستها. من النتائج، تبين أن جرعة من (0.025) غرام / لتر ودرجة الحامضية (7) لتكون الأمثل فعالة في معالجة مياه الصرف.خلصت النتائج إلى أن معاملة مياه الصرف الصحي الرواسب اللاهوائية باستخدام أكسيد الحديديك (Fe_2O_3) بالاشتراك مع تكنولوجيا خلايا الوقود الميكروبية هو وسيلة فعالة لعلاج مياه الصرف الصحي الرواسب اللاهوائية.

الكلمات الرئيسية : خلايا الوقود الميكروبية, المواد النانوية, معالجة المياه.

1. INTRODUCTION

Efficiently making use of biological processes to recover useful energy from organic wastes is always a goal for the wastewater treatment industry. In the study, microbial fuel cells (MFCs) are considered to be a very popular and promising bio-electrochemical power source for directly recovering electrical energy from carbohydrates as well as organics in wastewater. The application of MFCs in a wastewater treatment process has several advantages over existing processes. In addition to energy recovery as electricity in a wastewater treatment process, MFCs generate less excess sludge in a more stable condition than the aerobic treatment process **Greenman et al., 2009.**

The goal of waste water treatment facility is to reduce organic and inorganic materials in wastewater to a level that no longer supports microbial growth and to eliminate other potentially toxic materials. The efficiency of treatment is expressed in terms of reduction in BOD the relative amount of dissolved oxygen consumed by microorganisms to completely oxidize all organic and inorganic matter in the water sample. The higher the levels of oxidizible organic and inorganic material in the wastewater it will result in high BOD **Kargi et.al 200**.

Nanoparticles are materials having a size in the range of 1–100 nm. Iron oxide, titanium dioxide, fullerenes and carbon nanotubes have been made into nanoparticles **Boxall A.B. et. al 2007**, and **Christian.P. et. al 2008**. Fe_2O_3 is an effective reducing agent and catalyst for various applications in environmental remediation.

The heterogeneous reaction using Fe2O3 involves five steps: (i) mass transfer of the reactant to the Fe_2O_3 surface from the bulk solution; (ii) adsorption of the reactant on the Fe_2O_3 surface; (iii) chemical reaction at the Fe_2O_3 surface; (iv) desorption of the reaction product from the Fe_2O_3 surface; and (v) mass transfer of the product into the bulk solution **Lin. A. et. al 2008**.

The disposal of wastewater containing toxic organic compounds by the industrial community has been increased significantly in the recent past. So the treatment of such wastes generated from the industries is considered necessary as well as important in every aspect. Untreated wastewater if allowed to accumulate, leads to the decomposition of organic material and production of toxic gases. In industrial wastewater treatment, the objective is to remove or reduce the concentration of organic and inorganic compounds **Concetta and Cristina et. al 2005**.

In this study the use of (0.025gm) of Fe_2O_3 nanoparticles in enhancing the power output and wastewater treatment using microbial fuel cell technology was investigated. It proves to be a eco-friendly method along with the renewable source for generating electricity. The nanoparticles are characterized using X-ray Diffraction (XRD) and Scan Electron Microscopy (SEM), while the voltage and current was measured using Multimeter.

2.METHODS AND MATERIALS

2.1. Wastewater Characteristics

Wastewater (Anaerobic sludge) was obtained from Koyembedu sewage treatment plant, Chennai, Tamilnadu, India. Sample was stored in deep freezing unit at -20°C during the investigation. Initial values of the characteristics of wastewater are presented in **Table1.**

2.2. Preparation of Fe_2O_3 Nanoparticles

The Fe_2O_3 nanoparticles were synthesized by the well known liquid phase reduction method. 32.31 g of $Fe(NO_3)_3.9H_2O$ was completely dissolved in 400 ml of deionized water to form a 0.2 M solution and 28.77 g of NaOH was completely dissolved in 1200 ml of deionized water to form a 0.6 M solution. This solution was added drop wise into the above solution. After addition, this reaction continued with constant stirring. The solution was washed with deionized water and then dried in vacuum. The reaction is as follows:

$$Fe\ (NO_3)3.9H_2O + 3NaOH + H_2O \rightarrow FeOOH + 3NaNO_3 + 10\ H_2O \qquad (1)$$

2.3. Construction of Microbial Fuel Cell (MFC)

A sequential anode-cathode two chambered microbial fuel cell (MFC), in which the Fe_2O_3 (heated and non heated) of anode chamber was used as continuous feed for an aerated cathode chamber, was constructed in this experiment to investigate the performance of brewery wastewater treatment in conjugation with electricity generation. using autoclavable bottles each with diameter 30 mm and 100 mL capacity were taken. Two holes of diameter 5.5 mm and 1.5 mm were made on each of the lids for the insertion of the salt-bridge and electrodes. In the anode container, 100 mL of the Anodic Inoculation was used and in the cathode container 100 mL Potassium permanganate (0.1M) solution was used. The container lids were closed and sealed with tape. Salt-bridge was made with potassium chloride and agar in a 5 mm diameter level tube. Graphite sheets of 0.2 mm (thick) X 50 mm (length) X 12.5 mm (breadth) were used as electrodes. The electrodes were first soaked in 100% ethanol for 30 min. After that the electrodes were washed in 1 M Hydrochloric acid followed by 1 M Sodium hydroxide, each for 1 hr. They were then stored in distilled water before use. The electrodes were suspended using copper wires which were used to connect the conducting electrode and the multimeter. The cell was connected with a 10 ohm resistor to complete the circuit. The voltage and current where measured using UNITYDT-830D mutlimeter.

All operations were carried out at room temperature of 28°C. The variation in pH where (3, 5, 7 and 10) of the wastewater sample and was carried out by using 1N (HCl) and 1 N (NaOH).

2.4. Analytical Methods

Voltage (U) yielded from MFC for long time operation was recorded automatically by a computer and converted to power density **Wang et. al 2008**, according to:

$$P\ (W\ m^2) = U * j \qquad (2)$$

Where j is current density (A\ m^2), which is calculated by:

$$j = U/(R*A) \qquad (3)$$

Based on external resistance R (**Ω**) and projected surface area of cathode,

$$\text{Total Surface area} = 2\ (L*B + L*T + B*T))\ A\ (m^2) \qquad (4)$$

2.5. Analysis of Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD)

The BOD analysis was done using Young, J.C. procedure with 5 days incubation. COD analysis was done using open reflux method.

The % COD remaining was calculated by the following equation.

$$\%COD\,remaining = 100 - \left(\frac{initial\ COD - final\ COD}{initial\ COD} X\,100 \right) \qquad (5)$$

3.RESULTS AND DISCUSSION

3.1. Characterization of Fe_2O_3

Fig.1 (a) shows the X-ray diffraction pattern of the as-prepared Fe2O3 sample and **Fig.3** (b) shows the X-ray diffraction pattern of Fe2O3 annealed at 300°C. It can be indexed as the orthorhombic system by comparison with data from JCPDS NO: 81-0463 (α-FeOOH). The diffraction peaks at $2\theta \approx 21.2, 33.3, 34.7, 36.6, 52.9, 58.9, 61.3$ correspond to (110), (130), (021), (111), (221), (151), and (250) planes of sample respectively (JCPDS no: 84-0713). The information on the particle size was obtained from the full width at half maximum (FWHM) of the diffracted beam using Debye–Sherrer formula. **Qusay J. Raaheed et. Al, 2011**:

$$Dp = \frac{0.89\,\lambda}{\beta \cos\theta} \qquad (6)$$

The sample displayed an average crystalline size of 5.65 nm. The application of scherrer's formula to the (313) reflection peak at $2\theta = 35.6$ indicated the formation of maghemite nanoparticles with approximately ≈ 24nm in mean diameter for the sample annealed at 300°C for 3h and annealed in an air atmosphere at 300 °C for 3 h, to get dark brown coloured nanocrystalline γ-Fe2O3 powders.

The scanning electron microscopy (SEM) image of synthesized Fe_2o_3 particles is shown in **Fig 2.** Results indicate that the synthesized Fe_2O_3 particles are almost spherical. **Fig.2 (a)** shows evenly distributed spherical particles approximately 30 µm in size, and **Fig.2 (b)**, under higher magnification, confirms the spherical shape and the size range of each particle. On the spherical particles there were threads-like or tube-like structures clearly visible in **Fig.2 (b).** These structures increased the available surface area of reaction.

3.2. Voltage and Current measurements:

Aerobic sludge is used to construct a MFC (Cell 1). The cells are connected with a constant load of 10 Ω and periodically monitored for the voltage and current outputs and tabulated. The power density and current density area were calculated respectively.

Similarly there are two other cells constructed as above using aerobic sludge with heated and non heated and designated cell 2 and cell 3 respectively.

The following are the results obtained. In a normal double-chamber MFC, the highest current was observed at neutral pH (between 6.5 and 8) **Jadhav and Ghangrekar et.al, 2009**. In this study using Fe_2O_3 (heated and non heated) the current was higher at pH 5 and pH 10 respectively. This difference is due to the influence of the chemical substance added to the wastewater. The current density and power density too show the same pH and give best results as that of the current and voltage.

4.DISCUSSION

Large part of energy carried by the organic contaminants in wastewater is converted into electricity; MFC might produce less excess sludge, when used as a wastewater process, than the conventional aerobic process. For this reason MFC is a novel wastewater treatment process. **Kim et.al, 2004**. During operation, both the fuel cells anode chamber were continuously monitored for substrate (as COD) removal to enumerate the potential of fuel cell to act as wastewater treatment unit. Both the systems showed their potential for substrate removal indicating the function of selectively enriched mixed microflora in metabolizing the carbon source as electron donors. Relatively higher substrate removal efficiency and substrate degradation rate (SDR) was documented with ferricyanide cathode. During the stable phase of operation, COD removal efficiency of 74.20% and 74.15% a ccounting for SDR of 0.559 kg COD/m3 day and 0.464 kg COD/m3 day was observed for FC and AC respectively. Time taken for carbon exhaustion was relatively more in aerated cathode.

The voltage and current were measured at regular intervals and plotted for each pH **Figs. 3.a and 3.b.** Power density was then calculated and plotted against current density **Figs. 4.a and 4.b.** As show in (fig 5.a and 5.b) a reduction of more than 50% was observed in both the cases.

The MFCs might produce a far less excess sludge when used in the wastewater treatment process, than the conventional aerobic process. In view of this advantage, the MFC was proposed as a novel wastewater treatment process. **Kim et al., 2004.**

5. CONCLUSION

In the present investigation, electricity could be successfully generated from wastewater treatment as it provides a new technology in making the wastewater treatment more affordable for both the developing and the countries. Thus, this combination of wastewater treatment along with electricity generation offers a technology that is affordable and is ecofriendly which might fulfill the needs of the developing nations in the present scenario. The Fe_2O_3 particles prepared through a liquid-phase reduction method the calculated cell parameters are. According to the scherrer's equation the average crystallite size of the product was calculated to be about 35.6 nm as prepare and 24nm for the sample annealed at 300°C for 3hr. The precipitation method led to the formation of α-FeOOH. At temperature around 300°C α-FeOOH decomposes and diffraction peaks corresponding to Maghemite appeared. crystallinity increases. SEM analysis shows that the particles are spherical shape. Further the wastewater with nanoparticle was adjusted at various pH levels revealed that the optimum initial pH for better degradation was found to be pH 5 showed best results for power output and pH 7 showed best reduction in BOD and COD proving high wastewater treatment efficiency percentage. A high current density and power density was obtained at pH 5 and pH 10 for the non heated and heated Fe2O3 respectively. But the reduction in BOD and COD was obtained at pH 7 in case of non-heated Fe2O3 and COD reduction was obtained at pH 3 and BOD at pH 7 for heated Fe2O3. A large part of the energy stored by the organic contaminants in the wastewater is converted into electricity.

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NOMENCLATURE

COD	-	chemical Oxygen Demand.
BOD	-	Biological Oxygen Demand.
XRD	-	x-ray Diffraction.
SEM	-	scanning electron microscopy.
D_p	-	average crystallite size.
B	-	Line broadening in radians (FWHM of diffraction peak).
θ	-	diffraction angle.
λ	-	x-ray wavelength.
j	-	current density.
R	-	resistance.
U	-	voltage.
p	-	power density.
W	-	watt.
B	-	breath.
L	-	length.
T	-	width.
A	-	Amper.

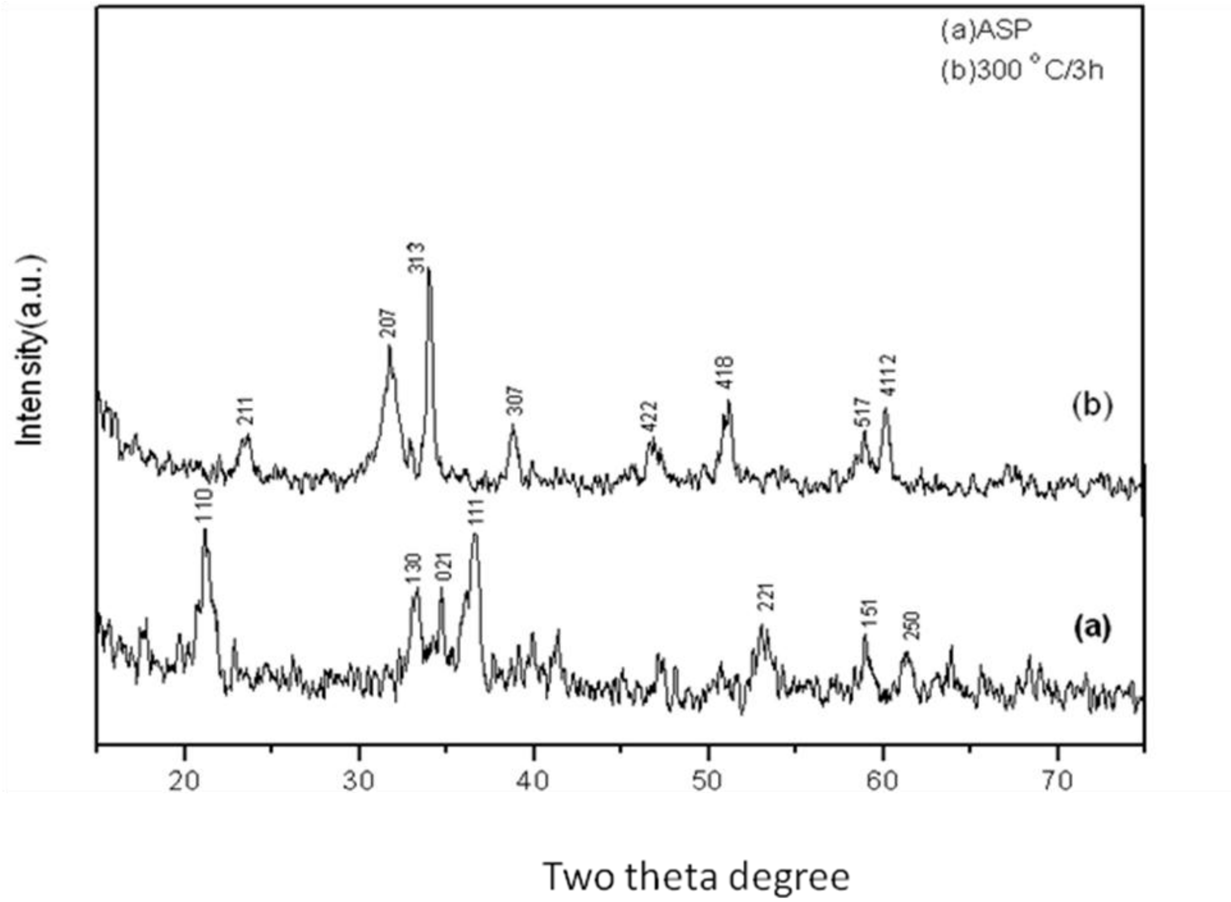
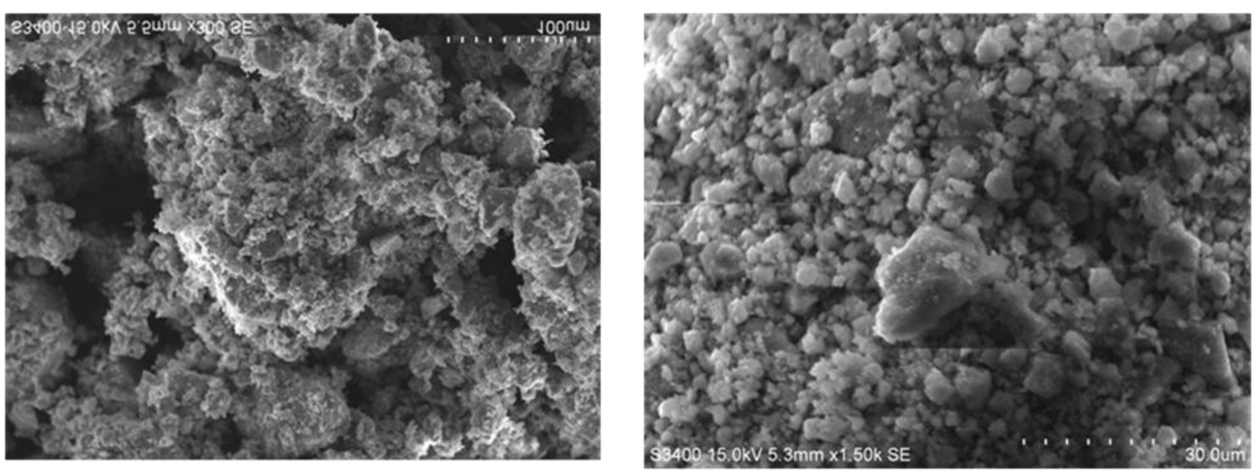


Figure 1. X-ray diffraction pattern of the as-prepared Fe2O3 sample.



(a) Heated

(b) Non Heated

Figure 2. SEM Image of heated Fe2O3and non heated Fe2O3.

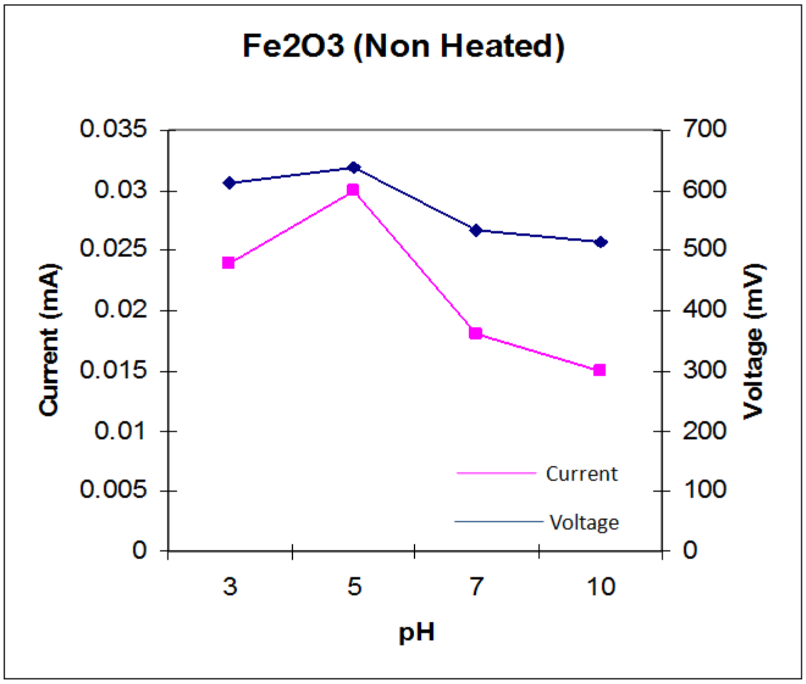


Figure 3.a. Maximum current and voltage produced at different pH using 2.5% (0.025 gm) of the nanoparticle.

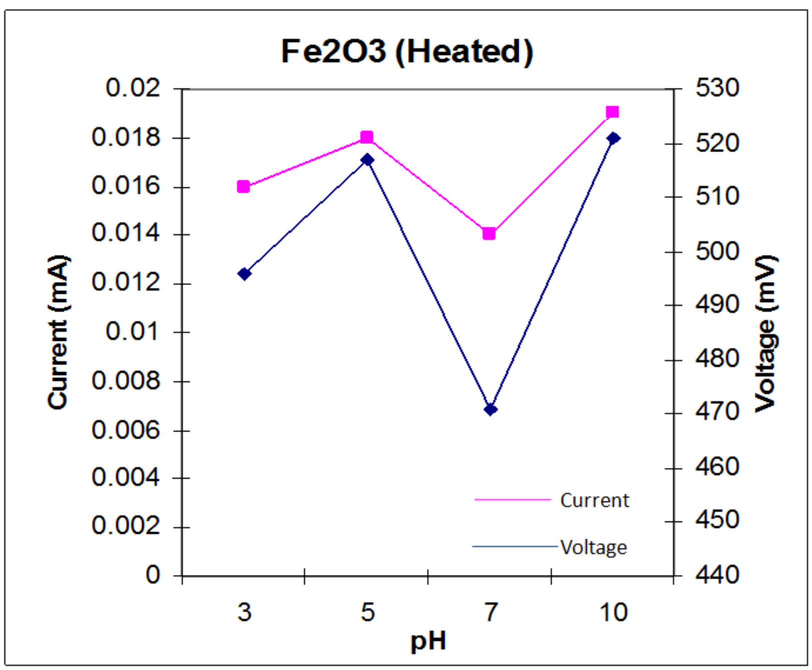


Figure 3.b. Maximum current and voltage produced at different pH using 2.5% (0.025 gm) of the nanoparticle.

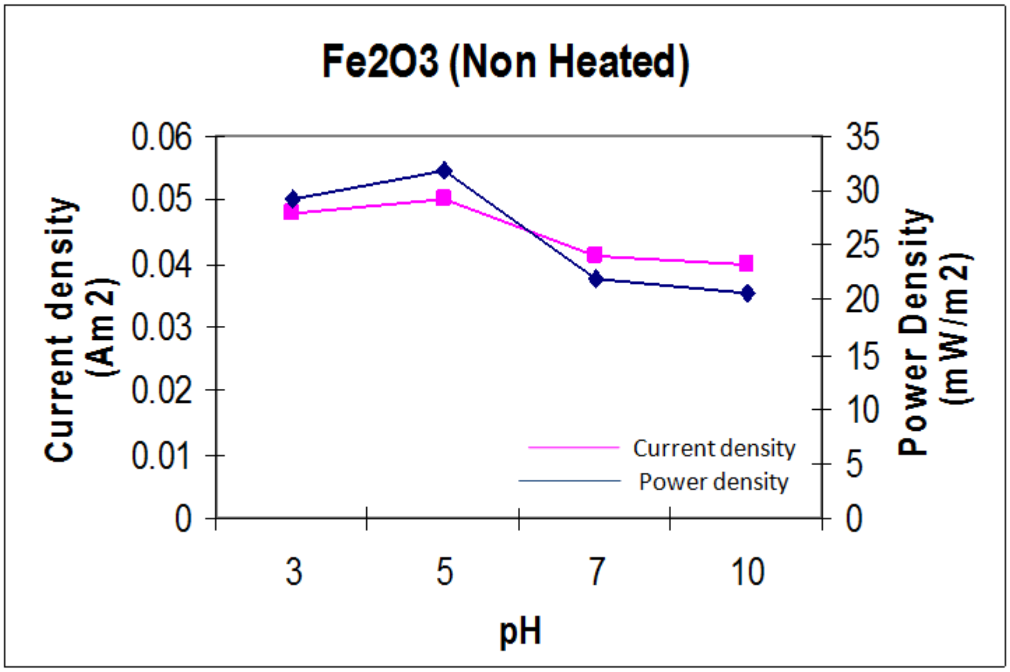


Figure 4.a. Maximum current density and power density produced at different pH using 2.5% (0.025 gm) of the nanoparticle.

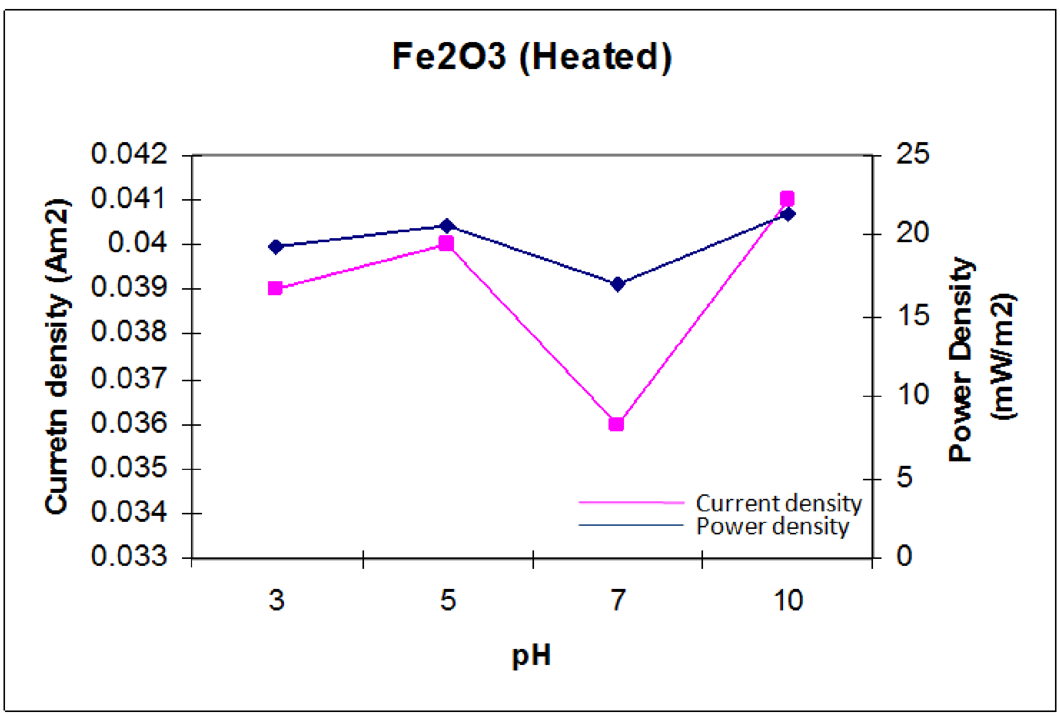


Figure 4.b. Maximum current density and power density produced at different pH using 2.5% (0.025 gm) of the nanoparticle.

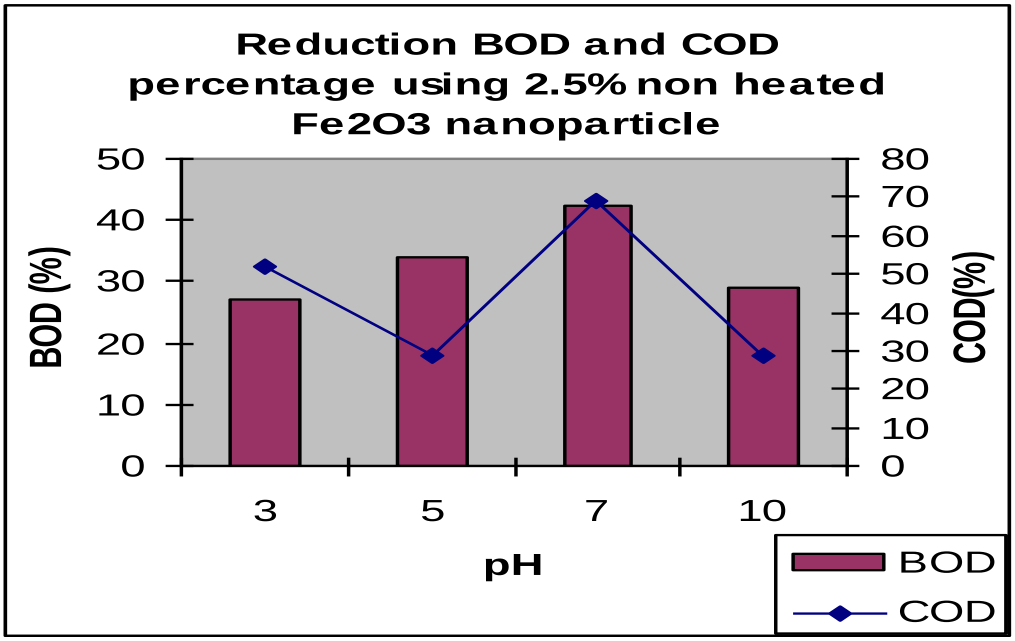


Figure 5.a. BOD and COD reduction at different pH using 2.5% (0.025 gm) of the nanoparticle.

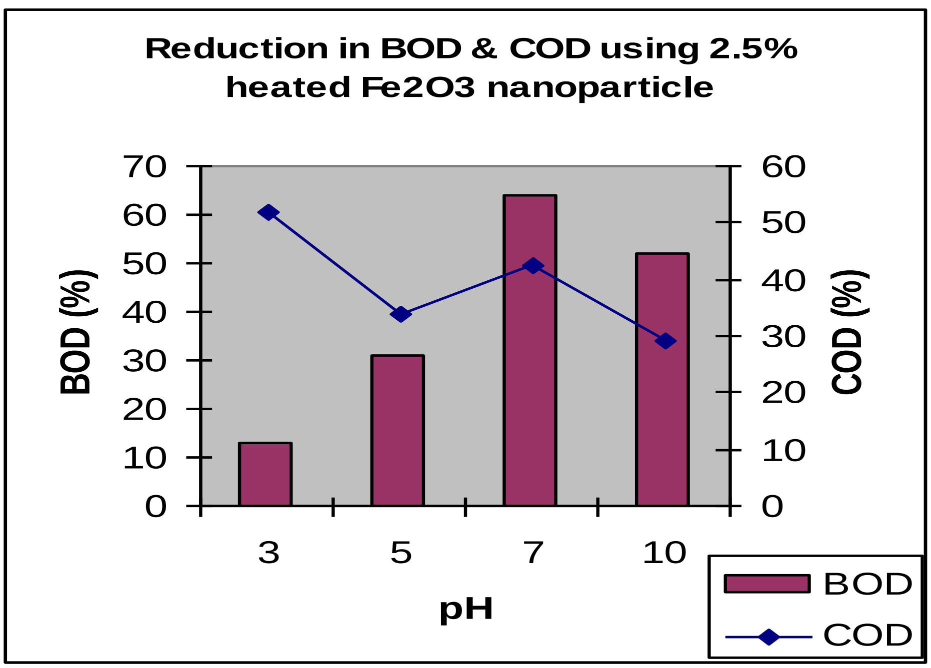


Figure (5.b) . BOD and COD reduction at different pH using 2.5% (0.025 gm). of the nanoparticle.

Table1. Characteristics of wastewater.

Parameters	Value
COD (mg/L)	15,000
Initial pH	7.0
Initial DO(mg/L)	2.2
Total Solids (mg/L)	1700
Dissolved Solids(mg/L)	750
Suspended Solids(mg/L)	1100