



Hybrid Process of Electrochemistry with Magnetite Nanoparticles for Treatment of Turbid Water

Thamer Jasim Mohammed¹, and Hadeel Atiya Al-Zuheri^{2,*}

¹ Department of Chemical Engineering, University of Technology, Baghdad, Iraq, thamer_jasim58@yahoo.com

² Department of Chemical Engineering, University of Technology, Baghdad, Iraq, che.80318@uotechnology.edu.iq

* Corresponding author: Hadeel Atiya Al-Zuheri, email: che.80318@uotechnology.edu.iq

Published online: 31 August 2019.

Abstract— Magnetic nanoparticles are now being investigated widely in field of water treatment. The aim of this study was to evaluate the feasibility of electrocoagulation process combined with addition of magnetite nanoparticles as a turbidity removal process. Bentonite was used as source of turbidity for the synthetic turbid water. Experiments were conducted in a bench scales electrocoagulation reactor where voltage was applied across a perforated plate of aluminum as anode, and iron mesh as cathode. Commercial grade of magnetite (Fe₃O₄) with an average nanoparticle size of 50 nm was used. The effect of some factors such as initial pH of the solution (5-9), current density (5-25 mA/cm²), and magnetite dosage (0.4-2.5 gm) on the efficiency of the process were studied. The residual turbidity obtained by using electrocoagulation process alone was (7.47 NTU) from initial turbidity of (200 NU) at constant conditions of pH 6, current density 15 mA/cm² and electrolysis time 20 min. While under these same conditions the combined electrocoagulation + magnetite process with the added (1.4 gm) of magnetite and under the same operating conditions the residual turbidity was (4.34 NTU), which indicate that the magnetite nanoparticles enhanced the electrocoagulation process.

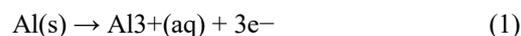
Keywords— Electrocoagulation, Magnetite, Water treatment, Turbidity.

1. Introduction

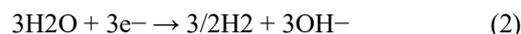
Turbidity is one of the main problems in the water treatment field. Turbidity is produced through the existence of clay or/and different colloidal components in water such as organic particles, soluble substances, and algae. These colloids have stability which make them cannot be sedimented. Thus, agglomerate small particles to bigger flocs is needed so they can be removed by sedimentation [13]. Recently, electrocoagulation is having a noticeable role in the treatment of water since it offers several important benefits, for example easiness in operation, no addition of chemicals, quite compactness, and less sludge production [18]. Electrocoagulation process include the producing of aluminum or iron hydroxides flocs in the solution. In this process coagulant is formed in situ by the passage of current density through the sacrificial anode which leads to its dissolution [3]. Three steps occur during electrocoagulation a) electrolytic reaction at surface of the electrode, b) coagulants formation by electrolytic oxidation in aqueous phase and colloidal particles adsorption by the coagulants, and c) separation by sedimentation or flotation which is initiated

by the evolution of H₂ bubbles at the cathode. Therefore, it's important to choose the appropriate material for the anode. Iron or aluminum is usually used as sacrificial anode, since they are cheap, readily available [17]. When aluminum electrode is used in the EC process, the main reaction in the anode will be [15]:

At the anode:



At the cathode:



The produced Al³⁺ from reaction (1) react with water and OH⁻ to generate different monomeric constituents, based on the pH of solution, finally they convert to Al(OH)₃ based on the kinetic of complex reactions. In the solution the total reaction will be as [15]:



Poly-hydroxides and hydroxides which have been formed, will stay as gelatinous suspensions in the solution, that they can cause destabilization of the emulsion by the neutralization of the colloidal charges [1]. However, because of the various composition of wastewater, conventional processes are insufficient and cannot be utilized separately in full scale. Scientists are trying to purpose combination between the methods of treatment to obtain high removal efficiencies of contaminants [5]. Combination of electrocoagulation with magnetite nanoparticles was used for the removal of arsenic from copper smelter wastewater [12]. These magnetic nanoparticles have high adsorption capacity and surface area, thus it may be utilized as a super adsorbent for pollutants separation from effluents and at the end they may be removed from solution by external magnetic field [8]. In this study magnetite nanoparticles (MNPs) are added to the electrocoagulation process to enhance the removal of turbidity from synthetic turbid wastewater. The effect of three factors on turbidity removal will be investigated: initial pH of solution, current density, and magnetite dosage.

2. Experimental work

2.1 Turbid water preparation

The turbid sample was prepared by mixing (0.3 gm) sodium bentonite with distilled water containing 1720 ppm dissolved NaCl by using high speed mixer of 2000 rpm to give water a turbidity of (200 NTU). Sodium bentonite was supplied by Research and Development Oil Center, Iraq. Turbidity in samples was measured before and after treatment by using Lovibond TurbDirect model /serial number 12/1805 with measurement unit NTU (Nephelometric turbidity unit) within the range (0.00–1000) NTU.

2.2 Magnetite nanoparticle characteristics:

Commercial grade of magnetite nanoparticles with the characteristics listed in Table.1 was employed as the magnetic sorbent particles for the experiments. These nanoparticles were analyzed with scanning electron microscopy (SEM) Fig. 1. The micrograph of bare magnetite particles showed that magnetite is in the nano-scale and have spherical shape with a diameter 50 nm. The pH of zero-point charge (pHpzc) of magnetite nanoparticles were measures so as to understand the charge of the adsorbent surface. Zeta potential of magnetite solution at different pH values was measures in (Iraqi Ministry of Higher Education and Scientific Research) using NanoBrook ZetaPALS Potential Analyzer

Table 1: Magnetite Characteristics

| Magnetite | Properties |
|------------------|--------------------------------|
| Chemical formula | Fe ₃ O ₄ |
| Molecular Weight | 536.39 |
| Radius | 50 nm |
| Purity | 99.9% |
| Shape | Sphere |
| Color | Black |

2.3 Experimental Set-up

As shown in Fig. 3 and Fig. 4, experiments were conducted in a batch electrocoagulator consisted of a Perspex compartment with total volume 2.5 liters and dimensions 20 cm in length, 14 cm in width and 16 cm height. Perforated aluminum plate and iron mesh (150 mm in length, 45 mm in height and of 0.4 mm thickness) was used as anode and Cathode respectively. The active area of anode was 89.29 cm² and the distance between electrodes was 3 cm as in [16].

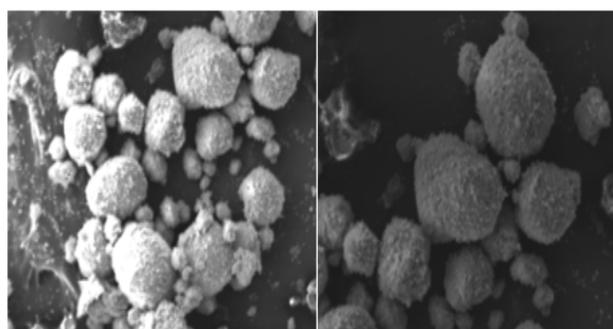


Figure 1: SEM images of magnetite nanoparticles.

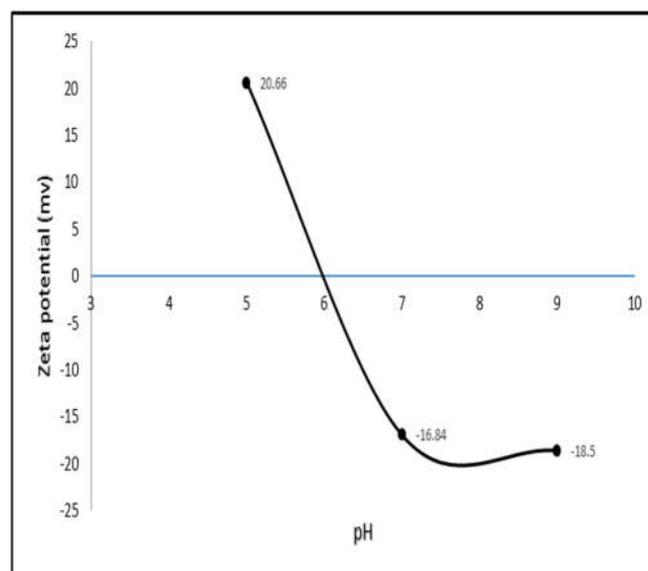


Figure 2: Zeta potentials of magnetite nanoparticles at different pH values.

A DC power supply (MODEL: APS3005S) with variable output of (0-30 V), and current (0-5 A) was used as direct current source

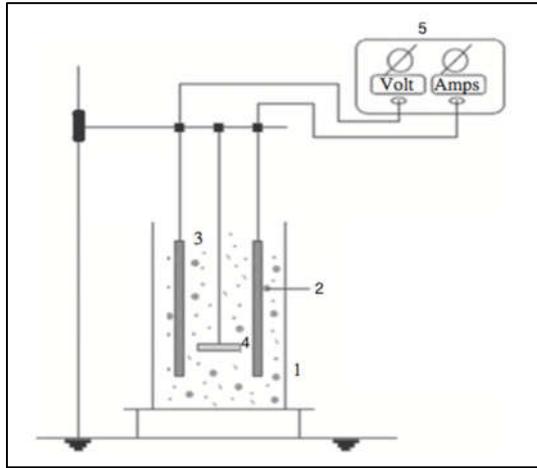


Figure 3: Experimental set up

2.4 Experimental procedure

The experiments were done by introducing 1500 mL wastewater samples to the batch reactor for each experiment. The influence of three factors on the removal efficiency of turbidity was examined at five different level as shown in Table. 2. The pH of the solution was changed by using of (0.1N) HCl and (0.1N) NaOH. To ensure good mixing, mechanical stirrer was used at 150 rpm [2,7]. Magnetite nanoparticles were added at different dosage to the center of the vortex before connecting the DC power to the electrodes, and allowed to contact

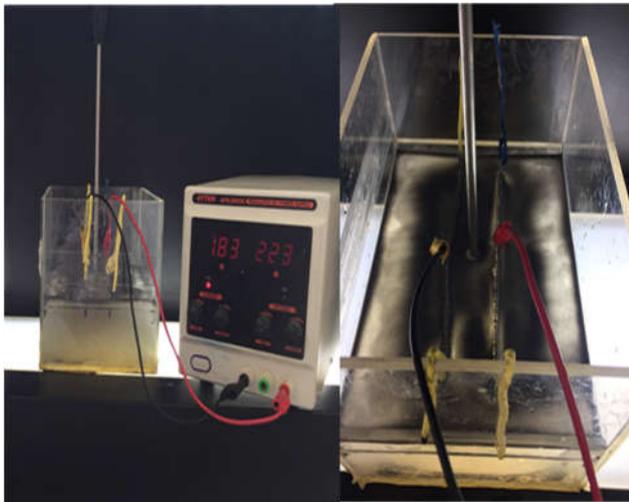


Figure 4: Photographic picture of the experimental set up

with the turbid water for adsorption to take place at 300 rpm and for 3 min [9]. After the end of each experiment, the treated water was allowed to settle for (10 min) [10]. Then samples were collected from fixed position between the cathode and anode about (3 cm) below the water surface to avoid collecting sediment floc from the bottom

and floated floc from the top of the water. Removal efficiency of the oil was computed as follows:

$$\text{Removal efficiency} = (C_0 - C_e) / C_0 \cdot 100 \quad (5)$$

Where C_0 is the initial turbidity (NTU) and C_e is turbidity at any time.

Table 2: Studied Factors and theirs corresponding levels

| Factors | Factors level | | | | |
|---------------------------------------|---------------|-----|------|------|-----|
| | 5 | 6 | 7 | 8 | 9 |
| pH | 5 | 6 | 7 | 8 | 9 |
| Current density (mA/cm ²) | 5 | 10 | 15 | 20 | 25 |
| Magnetite dosage (g/L) | 0.27 | 0.6 | 0.93 | 1.26 | 1.6 |

3. Results and Discussion

3.1 Effect of initial pH:

In order to study the effect of the pH on turbidity removal, experiments were performed by adjusting the initial pH to five different values of (5, 6, 7, 8, and 9). Figure (5) shows a comparison for EC process alone and the combination of EC + magnetite. In both processes the minimum residual turbidity was obtained at neutral pH 6-7, the residual turbidity then started to increase as the pH increased. This is due that aluminum hydroxide $Al(OH)_3$ is produced at pH (6-7) which is a precursor for the removal of turbidity by coagulation and its insoluble form of (Al^{+3}) . The increase in final turbidity at basic acidic medium, is because of the aluminum hydroxide $Al(OH)_3$ amphoteric state that becomes more soluble as the surrounded medium becomes more acidic or alkaline [4]. As shown in Fig. 5 the EC process gave a final turbidity at pH= 6 of 7.47 NTU, while in the EC+ magnetite process, residual turbidity at the same conditions was 4.34 NTU which indicate the adsorption of pollutants by the magnetite nanoparticles. The uptake of magnetite nanoparticles for the turbidity decreased as pH increased.

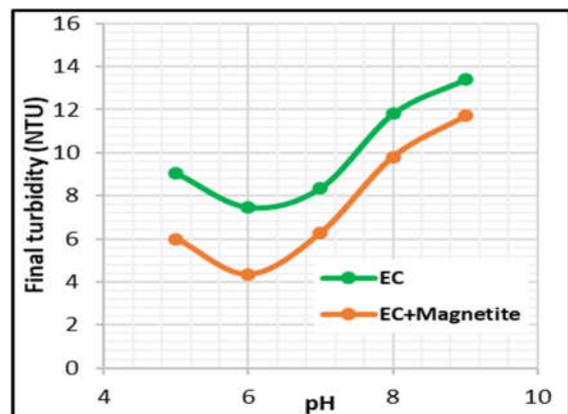


Figure 5 :Comparison of the effect of pH on final turbidity between EC and EC + magnetite process [Current density= 15 mA/cm², Time= 20 min, magnetite dosage= 1.4 gm, initial turbidity= 200 NTU]

It appears in Fig. 2 that the pHPZC of magnetite nanoparticles was equal to 6 which means below the pHPZC the surface charge density of magnetite becomes positive due to the protonation of magnetite nanoparticles, which favor the adsorption of negative charged turbidity due to electrostatic attraction [11]. But as observed at pH values higher than pHPZC turbidity removal is still happening by the magnetite nanoparticle which can be explained by that: the positive, negative, and neutral functional groups may exist together on the surface of Fe₃O₄. When pH < pHPZC, the groups of FeOH₂⁺ is more than the groups of FeO⁻, that mean even though there is positive charge on the surface of nanoparticles, the groups of FeO⁻ still exist and vice versa [6].

3.2 Effect of current density:

Five current densities (5, 10, 15, 20, 25 mA/cm²) were tested for the treatment of the turbid water. Results shown in Fig. 6 are expressed in form of the residual turbidity verses different values of current densities for both processes. The residual turbidity decreased as current density increased for both processes.

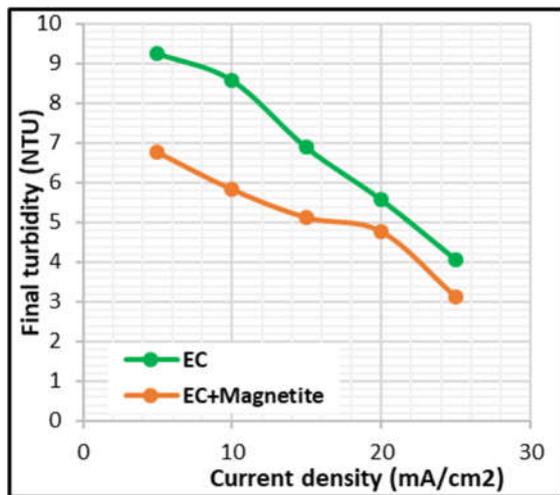


Figure 6: Comparison of the effect of current density on final turbidity between EC and EC + magnetite process [pH= 7, Time= 20 min, magnetite dosage= 1.4 gm, initial turbidity= 200 NTU]

This is because of the increase in the (Al³⁺) concentration and their hydroxide flocs that adsorb pollutants as current density increases according to Faraday's law, thus turbidity removal increased. Another effect of the high current density is the increase of rate of generation of the hydrogen bubbles and the decrease of their size that is beneficial for turbidity removal [14]. However, the residual turbidity achieved in EC process alone in (20 min) electrolysis time and (10 mA/cm²) was (8.59 NTU). While with the enhancing of the magnetite, the EC process obtained was (5.84 NTU) at the same condition. We can conclude from the comparison between EC and (EC + magnetite) processes in Fig. 6 that the adsorption of magnetite nanoparticles, decreased as the current density

increased. This may be attributed to the increasing in the formation of (OH⁻) at the cathode as current density increase which causes the deprotonation of the Fe-OH sites existing on the surface (Fe-OH=Fe-O⁻ +H⁺), and the formation of negative charge at the surface of nanoparticles and hence less adsorption [19].

3.3 Effect of magnetite dosage:

Figure (7) presents the effect of magnetite dosages (0.27, 0.6, 0.93, 1.26, and 1.6 g/L) on turbidity reduction. As the magnetite dosage increased, the final turbidity in the treated water reduced. In Fig. 6 it could be seen that the minimum residual turbidity was 2.33 NTU from initial turbidity of 200 NTU at magnetite dosage of (0.9 g) which means this is the optimum dosage. The increasing in magnetite dosage provides more surface area and thus more sites available for the adsorption of turbidity. But the increasing of the dosage behind the optimum level increase the probability of collision between the nanoparticles and thus particles aggregation is formed resulting in decreasing the total surface area and an increasing the diffusional path length, which both contribute to the decrease in the removal efficiency [20].

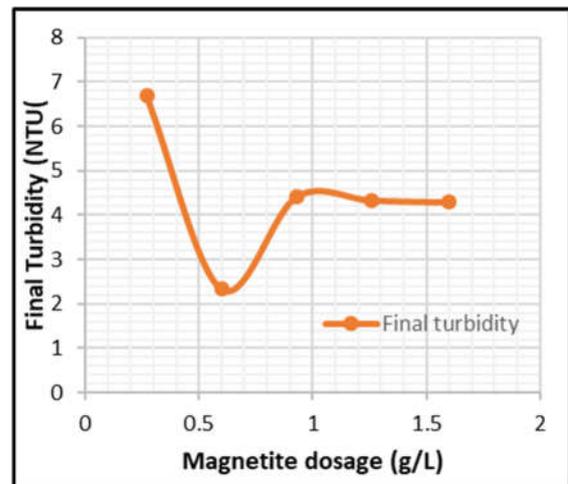


Figure 7: Effect of magnetite dosage on final turbidity between EC and EC + magnetite process [Current density= 15 mA/cm², pH= 7, Time= 20 min, initial turbidity= 200 NTU].

4. Conclusions

The present study attempted to investigate the applicability for the combination of electrocoagulation with magnetite nanoparticles in the removal of turbidity. The results showed that the EC process and magnetite adsorption both are affected by the initial pH of the solution. Optimum pH value was 6 and further increasing for the initial pH results in increasing the residual turbidity. Current density was also an important factor that the removal of turbidity increased by increasing current density, but it also affected the adsorption of the magnetite nanoparticles. The amount of the magnetite played a significant role too and the

optimum magnetite dosage was (0.9 gm) and further increasing led to increasing in the residual turbidity. Finally, the results proved that electrocoagulation process was enhanced successfully by the magnetite nanoparticles.

References

- [1] Abdel-Aziz, M. H., El-Ashtouky, E- S. Z., Zoromba, M. Sh., Bassyouni, M., (2016), "Oil-in-water Emulsion Breaking by Electrocoagulation in a Modified Electrochemical Cell", *Int. J. Electrochem. Sci.*, 11, 9634–9643.
- [2] Bayar, S., Yildiz, Y.S., Yilmaz, A.E., Irdemez, S., (2011), "The effect of stirring speed and current density on removal efficiency of poultry slaughterhouse wastewater by electrocoagulation method", *Desalination* 280 (1e3), 103e107.
- [3] Bazrafshan, E., Ownagh, K. A., & Mahvi, A. H., (2012) "Application of electrocoagulation process using Iron and Aluminum electrodes for fluoride removal from aqueous environment", *J Chem*, 9(4), 2297–2308.
- [4] Bensadok, K., Benammar, S., Lapicque, F. and Nezzal, G., (2008) "Electrocoagulation of cutting oil emulsions using aluminum plate electrodes", *Journal of Hazardous Materials*, Vol. 152, pp: 423–430.
- [5] El-Naas, M.H., Alhajja, M.A., Al-Zuhair, S., (2014), "Evaluation of a three-step process for the treatment of petroleum refinery wastewater", *J. Environ. Chem. Eng.* 2, 56–62.
- [6] Erto, A., Moreno-piraján, J. C., & Moreno-piraja, J. C., (2013), "Magnetite nanoparticles for removal of heavy metals from aqueous solutions: Synthesis and characterization".
- [7] Farrokhi, M., Hosseini, S., & Yang, J. (2014), "Application of ZnO – Fe₃O₄ Nanocomposite on the Removal of Azo Dye from Aqueous Solutions: Kinetics and Equilibrium Studies".
- [8] Gallo, J., Long, N. J., Aboagye, E.O., (2013), *Chem. Soc. Rev.* 42, 7816–7833.
- [9] Li, Y., Wang, J., Zhao, Y., & Luan, Z., (2010) "Research on magnetic seeding flocculation for arsenic removal by superconducting magnetic separation", *Separation and Purification Technology*, 73(2), 264–270.
- [10] Mehtap, G., (2009) "A Parametric comparative study of electrocoagulation and coagulation of aqueous suspensions of kaolinite and quartz powders", PhD. thesis, the Graduate school of Natural and applied sciences of middle east technical university
- [11] Nassar, N., (2012) "Iron Oxide Nanoadsorbents for removal of various pollutants from wastewater: An overview", *Application of Adsorbents for Water Pollution Control*, (July), 81–118.
- [12] Nuñez, P., Hansen, H., K., Aguirre, S., Maureira, C., (2011), "Electrocoagulation of arsenic using iron nanoparticles to treat copper mineral processing wastewater", *separation and Purification Technology* 79, 285–290
- [13] Rahmani, AR., (2008), "Removal of Water Turbidity by the Electrocoagulation Method", *J Res Health Sci*, Vol. 8, No. 1, pp. 18-24.
- [14] Safari, S., Azadi Aghdam, M., & Kariminia, H. R., (2016) "Electrocoagulation for COD and diesel removal from oily wastewater", *International Journal of Environmental Science and Technology*, 13(1), 231–242.
- [15] Shalaby, A., Nassef, E., Mubark, A., Hussein, M., (2014), "Phosphate removal from wastewater by electrocoagulation using aluminium electrodes", *American Journal of Environmental Engineering and Science* 2014; 1(5): 90-98
- [16] Thamer J.M, Esraa R.A & Thabit A.A "The 3rd International Conference on Building, Construction and Environmental Engineering (BCEE.3-2017) 23-125/10/2017 University of Technology and University Manofia Egypt.
- [17] Tir, M., and Moulai-Mostefa, N., (2008) "Optimization of Oil Removal from Oily Wastewater by Electrocoagulation Using Response Surface Method," *Journal of Hazardous Materials*, Vol. 158, No. 1, pp: 107-115
- [18] Ucar, C., Baskan, M.B., Pala, A., (2013), "Arsenic removal from drinking water by electrocoagulation using iron electrodes", *Korean Journal of Chemical Engineering* 30(10):1889-1895
- [19] Wang, X.S., Lu, H.J., Liu, F., Ren, J.J., (2011), "Adsorption of lead(II) ions onto magnetite nanoparticles", *Adsorpt. Sci. Technol.* 26, 407–417.
- [20] Yu, X., (2017), "Impact of environmental conditions on the sorption behavior of Pb (II) in Na-bentonite suspensions". *Journal of Hazardous Materials*, 183(1–3), 632–640.

عملية تهجين التخثر الكهربائي مع جزيئات المغنتيت النانوية لمعالجة المياه العكرة

د. ثامر جاسم محمد¹، هديل عطية عبد الكاظم^{2*}

¹قسم الهندسة الكيميائية، الجامعة التكنولوجية، بغداد، العراق، thamer_jasim58@yahoo.com

²قسم الهندسة الكيميائية، الجامعة التكنولوجية، بغداد، العراق، che.80318@uotechnology.edu.iq

* الباحث الممثل: هديل عطية عبد الكاظم، البريد الإلكتروني: che.80318@uotechnology.edu.iq

نشر في: 31 آب 2019

الخلاصة – مع التطور السريع في النانو تكنولوجي، يجري حالياً دراسة استخدام الجزيئات النانو المغناطيسية على نطاق واسع في مجال معالجة المياه. ان الهدف من هذا البحث هو تقييم جدوى عملية الدمج بين التخثير الكهربائي وجزيئات المغنتيت النانوية لإزالة العكورة. تم تصنيع مياه عكرة باستخدام البنتونيت كمصدر للعكورة. أجريت التجارب في مئخر كهربائي حيث تم تسليط الجهد عبر صفيحة مثقبة من الألمنيوم وهي الأنود، وشبكة مصنعة من الحديد وهي الكاثود. تم استخدام المغنتيت (Fe_3O_4) التجاري ذو متوسط حجم 50 نانومتر. تمت دراسة تأثير بعض العوامل التشغيلية مثل درجة الحمضية الابتدائية (5-9)، كثافة التيار (5-25 mA/cm²)، كمية المغنتيت المضاف (0.4-2.5 جرام) على كفاءة العملية. كانت العكارة النهائية التي تم الحصول عليها باستخدام عملية التخثير الكهربائي لوحدها (7.47 NTU) من عكورة أولية تقدر ب (200 NTU) في ظروف ثابتة من درجة الحمضية (6)، وكثافة التيار (15 mA/cm²)، وزمن تشغيل 20 دقيقة. في ظل هذه الظروف نفسها فإن عملية التخثير الكهربائي مع إضافة (1.4 غم) من المغنتيت كانت العكارة النهائية تساوي (4.34 NTU)، وذلك يشير إلى أن الجسيمات النانوية المغنتيت عززت عملية التخثير الكهربائي.

الكلمات الرئيسية – مغنتيت، الجزيئات النانوية، العكورة، معالجة المياه.