Research Article

Synthesis and characterization of α -Fe₂O₃/ γ -Fe₂O₃-nanoparticles from recyclable electro-coagulated sludge: insights and predictions for different application

Tadele Assefa Aragaw¹ · Belete Asefa Aragaw²

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Abstract

This research work reports on the synthesis and characterization of iron oxide nanoparticles from sludge. Precipitates generated from the electro-coagulation process were collected, size reduced, beneficiated, and thermally treated in an inert atmosphere to form iron oxide nanoparticles. Structural, surface, and optical properties of raw and thermally treated sludge were examined using XRD, SEM, FTIR, UV/Vis, TGA/DTA, and Zeta Potential. The X-ray diffraction pattern confirmed that as the sludge is annealed at a temperature of 100, 300, 500, and 800 °C, the phase transformed to goethite, magnetite, maghemite, and hematite respectively. Pure hematite were formed at the highest temperature. The crystallite size of hematite nanoparticle was calculated using the two most intense diffraction peaks and found to be about 30.4 nm at 800 °C and 28.3 nm at 500 °C. The SEM micrograph for heat-treated powered has an irregular shape with rough and porous surfaces leading to the best adsorptive feature. The optical band gap was found to be 2.06, 1.98, and 2.00 eV for 300 °C, 500 °C, and 800 °C heat-treated samples respectively. These findings can be an input to the industrialists and environmentalists that controlled sludge recycling mechanisms during wastewater treatment is beneficial in terms of cost and sustainability. Furthermore, an integrated wastewater treatment system with resource recycling technology at the initial stage of the installation could be made.

✉ Tadele Assefa Aragaw, taaaad82@gmail.com | ¹Faculty of Chemical and Food Engineering, Bahir Dar Institute of Technology, Bahir Dar University, Bahir Dar, Ethiopia. ²Department of Chemistry, College of Natural Science, Bahir Dar University, Bahir Dar, Ethiopia.

Graphic abstract

Keywords Electro-coagulated sludge · α -FeO(OH) · α -Fe₂O₃ · γ -Fe₂O₃ · Heat treatment · Nanoparticle

1 Introduction

Nowadays, an important paradigm shift is necessary at multiple levels to advance sustainable environmental management services toward a circular economy in which wastewater and sludge from it are considered a valuable resource rather than a liability. Like that of energy, clean water, fertilizers, and nutrients can be extracted from wastewater, valuable materials from the waste sludge can be recycled and prepared for different application which is helpful to achieve the sustainable development goals (SDGs). Initiatives in the researchers, the industrials, policymakers, and governments are critical to address the sludge from wastewater treatment plants challenge and raise awareness about its potential resource. Especially, iron oxide and hydroxide contained sludge is the main constituent from electroplating, iron metallurgy, electrocoagulation, and the like processing factory wastewater treatment plants.

The main by-products of wastewater treatment with electrocoagulation process using iron electrodes are

ferrous hydroxide, ferric hydroxide, and iron oxyhydroxide [1]. Those different iron hydroxide species generation persuades electrophoretic clustering of negatively charged colloids in the nearby positively charged iron electrodes which form polyatomic surface complexation within the electrolyte, electric current and electrode interaction [2, 3] Organic contaminants having active functional groups adsorbed by iron hydroxide precipitate with in situ coagulation system by a weak Van der Waals forces. The precipitates, which are formed with electrochemistry principle, have the capability of removing the organic contaminants in such a way that iron hydroxide has driven electrostatic interaction by adsorbing to the surface of the precipitate products [4].

Internal interaction with other dissolved contaminants; like azo dyes which are a major contaminant in textile effluent, inorganic ionic compounds, and metal ions also have a contribution in situ electrocoagulation processes. As a result, heavy metals and other elements contained in the effluents [5] can take place hydrolysis and redox reaction to form coagulated flocs through a complicated

electrochemical and physicochemical interaction in the process. In addition to the conventional hydroxides of iron, ox-hydroxides of iron can have a chance to be formed and removed from the process as goethite α -FeOOH and lepidocrocite γ -FeOOH which can be used as a source for iron oxides production iron oxides like hematite, maghemite, and magnetite [5, 6].

The formation of different iron oxide nanoparticles through dehydration and thermal oxidation of iron hydroxides/Fe₃O₄ are processed with a range of temperature phase interchanges between magnetite (Fe₃O₄)–maghemite–(γ -Fe₂O₃)–hematite (α -Fe₂O₃) which can be determined with X-ray diffraction techniques [7, 8]. In the thermal treatment with a range of temperatures, magnetite can undergo oxidation and forms stable hematite α -Fe₂O₃ [9, 10]. Magnetite can be transformed first to γ -Fe₂O₃ from 200 to 400 °C, and with a subsequence, the temperature can be transformed to α -Fe₂O₃ starting from 550 °C and above. Thus, thermal treatment with a certain range affects a stepwise formation of maghemite and hematite family of iron oxides. With increasing the temperature, the oxidative transformation of magnetite into hematite favors and quantity of hematite dominates at high temperatures.

Iron oxides in a nanoparticle (magnetite and hematite) form have a wide-ranging usage for commercial as well as industrial applications through technological advancement, due to their pigmented feature, especially it has wide application in pigment manufacturing technology [11, 12]. Iron oxide nanoparticles enormous for biomedical applications due to their unique magnetic properties, nontoxicity, and biodegradability, superparamagnetic iron oxide nanoparticles, targeted drug delivery, therapy, and cell separation [13].

Most of the time, iron oxide nanoparticles having a magnetic nature, hematite and maghemite, have many applications for the industry and medicinal purpose as a catalyst ferrofluids, magnetic ink, and footage media [12]. Maghemite and hematite are excellent materials due to having low manufacturing costs and also are stable in the acidic solution media which can offer photocatalysis reaction, water-splitting technology, and gas sensors [14–17].

In the environmental remediation point of view, iron oxides carryout promising results as a catalyst and adsorbent. Adsorption of organic matter in the wastewater stream on magnetic powdered activated carbon was studied by Lompe et al. [18]. Also the adsorption potentials of electro-coagulated sludge, raw, and produced iron oxide nanoparticles after thermal treatment were investigated for direct red 28 dye [19]. The synthesis and properties of iron oxides and the raw EC sludge adsorbent for the removal of direct red dye are described in detail including its isotherm and kinetics phenomenon. The best removal efficiency was recorded with alternating various

parameters like solution pH, temperature, adsorption time, adsorbent dosage, and dye concentration. Another study by Mousavi et al. [20] of iron oxides and its modification with different materials for wastewater treatment is examined.

Recovery and investigating the surface and structural properties of electro-coagulated sludge from textile wastewater treatment plants which can be used for the different applications have promising advantages to the total sustainability of the environment in such a way that sludge waste management in the future and resource utilization. The present study focuses on the wet and thermal treatment mechanism of electro-coagulated sludge through a range of temperatures to produce valuable iron oxide nanoparticles. Also, chemical, surface, and structural characteristics of the raw EC sludge and produced iron oxide were investigated using FTIR, UV absorption, XRD, TGA/DTA, and SEM analytical techniques. This research work aims to study the recycling of EC sludge and surface and structural characterization of iron oxide nanoparticles through a range of temperatures.

2 Materials and methods

2.1 Overview of the electrochemical process

The electrocoagulation processes of a textile wastewater treatment plant have the so-called cascade electrochemical reactor. The system has two compartments as a coaxial flow electrochemical reactor, comprising of a central galvanized platinum as cathode and iron as an anode (plate iron sheet) having an anode-to-cathode surface spacing and electrode gaps.

The inlet and outlet of the system confirmed as a uniform fluid flow in the cascade reactor through the chamber as per the manufacturer's design and flushing of formed gases and solids are removed manually with skilled operators. Before the electrocoagulation unit processes, the textile effluent has a grit chamber unit process to remove the coarse particles and is homogenized from the equalization tank to neutralize the basic media and make the effluent suitable to the reactor. Concentrated sulfuric acid is added to the wastewater at the equalization tank to form a neutral environment to improve electro-oxidation processes and also can be able to dissolve the suspended materials which were not trapped at the grit chamber. The treatment system is a continuous having a recirculation system by one-third of the inlet volume at the manufacturer's design flow rate of 20–25 m³ h⁻¹ through the electrochemical reactor for the electrolyte (wastewater) TDS concentration above 500 mg/L. The cascade reactor is operated in galvanostatic mode at the 20–30 Amp/s

current density proportional to the inlet volumes of the wastewater with continuous treatment time (for $1 \text{ m}^3 \text{ h}^{-1}$) in a pH range of 6–7 at ambient temperature. The DC voltage is automatically changed based on the current density adjustment

2.2 Electrocoagulation mechanisms

The electrocoagulation (EC) processes is an electrochemical reaction which can produce coagulants and removing the suspended, colloidal, and dissolved materials for wastewater treatment. In the EC processes, the generation of coagulants by dissolution anodic electrodes with simultaneous formation of hydroxyl ions and hydrogen gas from the cathodic electrode. In the EC process, iron hydroxide and/or polyhydroxide precipitates are produced [21]. Some the dissolved organic impurities have been adsorbed on to the iron hydroxide and/or polyhydroxide precipitates and can be removed by beneficiation, and the thermal treatment [22]. The EC process generates three layers of iron hydroxide and/or iron oxide precipitates in different states of oxidation as shown in Eqs. 1–4 [21].

2.3 Sample collection and physical treatment

Sludge samples were collected from Bahir Dar Textile factory wastewater treatment plant, Bahir Dar, Ethiopia. It was dried with an oven at 70°C , ground and milled using a jaw crusher and disc mill. The desired product was used for soaking and oversize products have been returned to the crusher. For the separation of desired powered from grease, soluble salts, organics, the soaking was conducted. The powdered sludge was dispersed in de-ionized water for 24 h and banded to separate all floatable oils, specks of dust, and dissolved solid particles. With decanting the supernatant, the slurry was washed until the unstable suspended particle removed. The suspension after wet treatment was dried at 70°C to remove absorbed water, again dried, ground and milled to make fine powder for thermal treatment.

2.4 Thermal treatment

The high-temperature oxidative transformation of iron hydroxides/ Fe_3O_4 has followed a range of temperature-dependent phase interchanges from maghemite to hematite [8]. The anhydrous product from the physically treated EC sludge powered was sampled to a crucible cup and placed inside a muffled furnace. Nitrogen gas was supplied from external sources to the furnace with a flow rate of 100 min^{-1} for 20 min to make an inert atmosphere and was thermally treated with constant nitrogen flow at 10 min^{-1} for 3 h to remove organics from the sludge and oxidative transformations to hematite type of iron oxide nanoparticle. At each temperature (100 , 300 , 500 , and 800°C), the same treatment conditions and time were maintained. The mass loss as the organic carbon content of the dehydration from the sludge was determined by classical gravimetric analytical techniques and was recorded as less than 10%.

2.5 Surface and structural characterization

FTIR (JASCO 6600 typeA) spectrophotometer was used to determine the functional groups for raw and thermally treated (at 300 , 500 , and 800°C) EC sludge. The analysis was done at a wavenumber range of $400\text{--}4000 \text{ cm}^{-1}$. The powder sample with KBr was grounded uniformly using mortar and pestle and pelletized. Raw and thermally treated (300 , 500 , and 800°C) EC sludge were used for functional group determination. X-ray diffraction, XRD, is a method that can be used to detect the crystalline phases of the materials in it and for quantitative analysis. Particularly, it is used due to the superior highlighting of the dimensional atomic structure that has a direct implication on the characteristics of the nanomaterial. The crystalline and phase interchange were examined for both the raw and thermally treated (at 100 , 300 , 500 , and 800°C) EC sludge, and the diffraction patterns were measured using XRD (SHIMADZU, MAXima_X XRD-7000) with CuK radiation. XRD diffractograms were obtained between the X-ray intensity on the ordinate and the Bragg angle, θ , on the abscissa were performed on a $\theta\text{--}2\theta$ angle range between 10° and 80° through continuous scanning at a step size of 0.02° with a counting time of 1 s per step with a scan speed of $0.054^\circ/\text{s}$ at a 40 kV voltage and 30 mA current intensity with divergence slit: 1.0° , scatter slit: 1.0° , receiving slit: 0.30 (mm) . The surface morphology of the raw, as well as thermally treated, 500°C , EC sludge, were examined using scanning electron-microscope, Inspect™ Scanning Electron Microscope, SEM (INSPECT F50) with different magnification and scale bar. Zeta potential and Electrophoretic mobility measurements were done using a zeta potential meter (Malvern Zetasizer Nano ZS series)

at different pH values to determine the surface charge nature. The values were recorded 2, 4, 6, 8, 10, 11, and 12 pH values. It determines the electrophoretic mobility of the particles automatically in the powered and converts it to the zeta (ζ) potential values using Smoluchowski's Eq. 5 [23].

$$v_E = 4\pi\epsilon_0\epsilon_r\zeta/6\pi\mu(1 + \kappa r) \quad (5)$$

where ϵ_0 and ϵ_r are the relative dielectric constant and the electrical permittivity of a vacuum respectively, μ is the solution viscosity, r is the particle radius and $\kappa = (2n_0z^2e^2/\epsilon_r\epsilon_0k_B T)^{1/2}$ is the Debye–Hückel parameter, n_0 is the bulk ionic concentration, z is the valence of the ion, e is the charge of an electron, k_B is the Boltzmann constant, and T is the absolute temperature.

2.6 Thermal analysis

The raw electro-coagulated sludge mass loss by thermogravimeter, TGA was analyzed simultaneously with the phase transformations analysis using differential thermal analysis, DTA, through ATAT2012 equipment. The measurements were carried out from room temperature up to 1000 °C temperature ranges with air atmosphere in a flow rate of 10 and 20 mL/min on a sample mass of 15 mg. The thermogravimeter analyzed thermal accuracy and stability was calibrated by heating indium (melting point = 156.6 °C) as a standard at 10, 15, and 20 °C/min. The analysis was conducted using TGA–DTA emphasized their thermal stability and the mass loss through two curves simultaneously plotted based on the temperature profile.

Fig. 1 FTIR spectral analysis of raw and thermal treated at (300, 500, and 800 °C) EC sludge

2.7 Optical properties

UV–visible diffusion reflectance is important to determine the optical properties and the bandgap of the material. The diffusion reflectance spectra of the raw and thermally treated (300, 500, and 800 °C) electro-coagulated sludge was determined. The spectra was acquired using color-eye spectrophotometer (Color-Eye3100). Powdered electro-coagulated samples were pressed by hand with stainless steel washer for suitable pellet formation. The formed thick pellet with a support of the pellet holding materials were placed. BaSO₄ integrating sphere as 100% reflectance white standard were used. The Diffuse reflectance spectra were recorded from 400 to 700 nm.

3 Result and discussion

3.1 FTIR spectral analysis

FTIR spectra of raw and thermally treated (300, 500, and 800 °C) EC sludge with a scanning range of 4000–400 cm⁻¹ are depicted in Fig. 1. Bands appearing at 3439 and 2921 cm⁻¹ are for the stretching vibrations of O–H which is assigned to surface OH groups of ferric oxyhydroxide and iron oxide and C–H stretching respectively. Also, the peaks at 1632, 1430, 1097 and 872 cm⁻¹ are for the asymmetric and symmetric vibration in C=O stretching in the carboxyl functional group [24], N=N stretching bands, C–O stretching and N–H deformation in the amines respectively from the raw EC sludge. The absorption peaks at 3439 cm⁻¹ and 1632 cm⁻¹ after thermal treatment is also attributed to the water of hydration. The bending frequency of surface hydroxyl group was observed at 1392 cm⁻¹ and increases its peak intensity as the temperature increases which are similar to previous reports [25]. A small peak appeared at 881 cm⁻¹ and 1050 cm⁻¹ in the raw EC sludge were disappeared after thermal treatment. This is due to the adsorbed carboxyl and amine functional group in the dye molecule thermal decomposition. Most Azo N=N stretching bands occur between 1580 and 1400 cm⁻¹ which are shown in raw EC but disappeared from thermally treated. Also absorption bands at 3424 cm⁻¹ which may be attributed to the –NH₂ group, which overlaps with the stretching vibration of the OH groups. Also, the presence of the peak located around 2900 cm⁻¹ corresponds to C–H vibrations in the raw EC sludge tells that there is adsorbed organic carbon from the sludge but disappeared after thermal treatment [26, 27]. The bands appearing from 450 to 650 cm⁻¹ belongs to the Fe–O stretching vibration of Fe₂O₃ [28], indicating that iron oxide nanoparticles are formed after thermal treatment of magnetite and iron hydroxides. The band corresponding to Fe–O stretching

mode of $\alpha\text{-Fe}_2\text{O}_3$ is shown at 576 cm^{-1} having a sharp (high) intensity after thermal treatment at 500 and 800°C suggesting that the $\alpha\text{-FeOOH}/\text{Fe}_3\text{O}_4$ have undergone an oxidative transformation to maghemite and hematite. The peaks at about 455 for the samples treated at 500°C and 800°C , and 558 and 530 for the samples treated at 500°C and 800°C respectively, are assigned Fe–O vibrations which are characteristic vibrations bands at of intrinsic $\alpha\text{-Fe}_2\text{O}_3$ nanostructure [29, 30]. According to Chernyshova et al. the bands of hematite nanoparticle can vary within $662\text{--}526\text{ cm}^{-1}$ and $494\text{--}437\text{ cm}^{-1}$ ranges depending on the particle size and presence of impurities [31]. For example, Mohammed et al. [32] reported that Fe–O stretching vibrations are shifted toward lower wavenumber side up to Zn 4% and then shift to higher wavenumber for Zn 6% due to variation in cation-oxygen bond length. The band appearing at 1097 cm^{-1} is typically metal hydroxyl (M–OH) stretching vibration from raw EC sludge but disappeared after thermal treatment due to its transformation to iron oxide nanoparticles [33, 34]. Thus, thermal treatment of the EC sludge is important for the productions of the most valuable iron oxide, $\gamma\text{-Fe}_2\text{O}_3/\alpha\text{-Fe}_2\text{O}_3$ -nanoparticles from iron hydroxide/oxy-hydroxide and magnetite. According to the study by Ovcharenko et al. the formation of O-defect on $\alpha\text{-Fe}_2\text{O}_3$ during heat treatment at 800°C leads to dissociative water adsorption at oxygen vacancy sites where the OH– fills the vacancy position [35]. This could be the reason for intense OH bands of $\alpha\text{-Fe}_2\text{O}_3$.

3.2 X-ray diffraction analysis

The X-ray diffraction patterns recorded for electro-coagulated (EC) sludge from electrochemical unit processes

Fig. 2 X-ray diffraction pattern of raw and thermally treated ($100\text{--}800^\circ\text{C}$) EC sludge

of textile wastewater treatment plants are depicted in Fig. 2. The major diffraction patterns corresponding to $\alpha\text{-FeOOH}$ (goethite) are observed at $2\theta = 21.2^\circ$, 33.2° , and 36.5° whereas peaks at 18.4° , 30.2° , 35.6° , 43.2° , 53.5° , 57.2° , and 62.7° are due to Fe_3O_4 (magnetite) phase in raw and thermally treated at 100°C EC sludge. The formation of goethite (orthorhombic) and magnetite (cubic) phases are in agreement with ICSD reference code 01-081-0462 and 01-089-3854 respectively. The goethite phase disappeared when thermally treated with temperature 300°C and above. This is due to the transformation of $\alpha\text{-FeOOH}$ to magnetite, maghemite, and hematite. At 300°C , the XRD pattern displays major characteristic peaks due to magnetite situated at 2θ values of 30.2° , 33.4° , 35.7° , 43.2° , 53.5° , 57.1° , and 62.8° in agreement with ICSD reference code 01-089-3854 for cubic magnetite crystal. All the peaks are higher angle shifted to the reference. This is due to the oxidation of $\text{Fe}^{2+}\text{--Fe}^{3+}$ in the magnetite structure. Magnetite contains both Fe^{2+} and Fe^{3+} with 1:2 ratio ($\text{Fe}^{2+}:\text{Fe}^{3+}$). During heat treatment of magnetite, some of the Fe^{2+} could be oxidized to Fe^{3+} . Due to the smaller ionic radius of Fe^{3+} compared to Fe^{2+} , the crystal exhibit lattice contraction which results from a higher angle shift in diffraction measurement. At 500°C , the magnetite phase disappeared as a result of its oxidative transformation to the Fe_2O_3 phase. Diffraction angles at 30.3° , 35.6° , 43.5° , 54.0° , 57.4° , and 63.1° are due to maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and 33.2° , 35.6° , 49.5° , and 54.1° are due to hematite ($\alpha\text{-Fe}_2\text{O}_3$) phase according to ICSD reference code 00-025-1402 and 01-073-2234 respectively. Finally at 800°C maghemite is converted and a pure rhombohedral hematite phase is formed with no other impurities exhibiting sharp and strong peaks. All the peaks at 24.2° , 33.3° , 35.7° , 41.0° , 49.6° , 54.1° , 62.4° , 64.1° match well with hematite (ICSD reference code 01-079-1741). This shows the highly crystalline nature of the material formed which is one of the requirements for optoelectrical and catalysis applications.

A similar study was reported by Cho et al. [36]. The diffraction line $2\theta = 30.2$ and 43° from the raw to heat-treated up to 500°C indicates the inverse spinel iron ferrite (Fe_3O_4) structure and thermally treated at 700°C disappeared which suggests that the no ferrites can exist at high temperature [37, 38]. This suggests that ferrite is completely transformed into hematite. The XRD diffractograms in Fig. 2 obtained after thermal treatment with a range of temperatures illustrate that iron oxy-hydroxide and goethite (FeOOH) phases disappeared after 300°C and completely transformed to maghemite and hematite at 500°C and fully hematite at 800°C . The small peak detected at $2\theta = 29.7^\circ$ from the raw as well as thermally treated up to 500°C is due to the impurities of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ which were precipitated in situ in the effluent treatment [36]. Based on the Fe–O thermodynamic stability for different iron oxide

phases, within the temperature range where the particular phase of the material is stable, an increase in temperature increases the particle size due to agglomeration. But, across the phase transformation temperature, the recrystallization of the lattice atoms into a different structure happens with increasing temperature which leads to the formation of a different phase of the material. When crystal growth begins an assembly of primary particles that have grown together form agglomerates that later converted into a new larger particle (aggregate). Based on the XRD data, the crystallite size of hematite nanoparticle was calculated using the two most intense peaks and found to be about 30.4 nm at 800 °C and 28.3 nm at 500 °C using the Debye Scherer equation as shown in Eq. 2.

$$D = \left(\frac{0.9\lambda}{\beta \cos \theta} \right) \quad (6)$$

where D is particle size, λ is the wavelength of the X-rays = 0.154 nm, β is the full width at half-maximum of two most intense XRD peaks, in this case, K is constant = 0.9 and θ is the Bragg diffraction angle. As the temperature increases, the particle size increases due to agglomeration.

The reactivity and phase transformation of iron oxide changes with decreasing particle size as a result of contributions of such effects as larger surface area and kinetic advantages, the relative proportion of the catalytically active crystallographic facets and surface defects (kinks, edges, corners, vacancies) in the exposed surface, and the quantum-size effect. Size can affect both stoichiometry and structure of the nanocrystal interior and surface or can even cause local or integral phase transition [39]. As a consequence, the electronic band structure of iron oxide particle as a whole, and in particular it is acid–base and redox properties, are modified in a complex particle manner. Along with their dynamic character, these features

Fig. 3 SEM Micrographs of **a** raw, **b** heat-treated at 300 °C **c** heat-treated at 500 °C and **d** heat-treated at 800 °C electro-coagulated sludge

make a study of relationships between physicochemical parameters and chemical reactivity of iron oxide particles [31, 40]. Though XRD is a bulk analysis technique, it confirms us that hematite, maghemite, magnetite, and goethite were the only products detected for the thermally treated samples at 800 °C, 500 °C, 300 °C, 100 °C, and raw EC sludge which suggests that metal oxide impurity phases are negligible. In addition, the absence of heavy metal cation impurities is suggested based on the unavailability of XRD and FTIR peak shift caused by lattice expansion/contraction and vibrations as a result of different size cation impurity doping.

3.3 Surface morphologies

The scanning electron microscope, SEM, was also used to monitor the modifications in the sample morphology of raw and thermally treated electro-coagulated sludge. The raw and thermally treated electro-coagulated sludge resulted in a significant structural transformation are shown in Fig. 3a–d. The powered sludge is unstructured in nature, irregular in shape with uneven edge agglomerate and rough in the surface. Adsorptive and rough surface is observed, filling with many small grains of other iron oxides such as maghemite and hematite [41], and formed a complex structure. There is a notable difference in the micrographs obtained for both raw and thermally treated at 300 °C which are observed less rough than the samples treated at higher temperatures (500 and 800 °C) with a distinguishing appearance, characteristic of sintered material. High temperature treated samples (Fig. 3c, d) produced materials with more rough indicating better adsorptive nature compared to the raw and 300 °C treated sludge. This roughness could provide better adsorption property for high temperature treated samples. It suggests that removing the dissolved solids and organic contaminants from the matrix sludge resulted in more adsorptive, porous crystalline morphology of heat-treated but are amorphous morphology in the raw EC sludge. This is also confirmed with XRD diffraction patterns. It can be noticed that the oxidative transformation of iron hydroxide/oxyhydroxide and ferrite containing electro-coagulated sludge to maghemite and hematite through subsequent temperature. From the electro-coagulated metal hydroxide sludge, different elements detected and dominantly were iron about 83% as reported by Adyel et al. [42], out of the twenty-two elements that have been executed. It is aggregates, dispersive aggregates corresponding to the top surface layer of the powdered EC sludge products. Similar morphological structures of iron hydroxides and iron oxides were reported [34, 43, 44].

3.4 UV absorption

From the scattering theory, the shape of the spectra and wavelength of the maximum optical extinction depends on the dielectric function of the nanoparticles [45]. Due to the interaction of liquid molecules and charged nanoparticles in the media, electrical layers surround the surface of generated nanoparticles which makes the spectral pattern different [46]. Besides, due to having high dipole moment in liquid solvent sufficient electrostatic repulsive force occurs because of the overlying of a strong electrical layer. A similar report on zinc oxide nanoparticles with the effect of solvents, such as acetone, ethanol, and water for their optical and morphological properties has been reported [47]. Due to these problems, it is better to measure the diffuse reflectance spectra of solid samples than their liquid dispersion. Hence, the UV–Vis diffuse reflectance spectra of the electro-coagulated sludge material in the wavelength of 400–700 nm have been measured. The UV–visible spectra of solid raw and thermally treated electro-coagulated sludge were determined as shown in Fig. 4a. The diffuse reflectance spectra of samples treated at 300, 500 and 800 °C showed an abrupt change in loss of reflectance at about 620 nm, displaying the increased absorption of light by the material. The raw electro-coagulated sludge has not shown clear absorption onset relative to the heat treated samples. As iron electrodes are used during the electro-coagulation process, the sludge contains mixtures of iron hydroxide and oxyhydroxide. Thermal annealing of mixtures of iron hydroxide and oxyhydroxide produces different phases of iron oxide depending on the annealing temperature. This is confirmed from the XRD measurement. Pure α -Fe₂O₃ phases and 800 °C and mixture of α -Fe₂O₃ and γ -Fe₂O₃ were formed at 800 °C and 500 °C, respectively.

The optical bandgap of the synthesized samples was calculated from diffuse reflectance spectra using Tauc plot method and Kubelka–Munk model.

$$F(R) = \frac{(1 - R)^2}{2R}$$

$$(F(R)h\nu)^n = k(h\nu - E_g) \quad (7)$$

where $F(R)$ represents the Kubelka–Munk function, E_g is the bandgap energy, $h\nu$ is the photon energy, R is reflectance and k is a constant [48]. The optical band gap was found to be 2.06, 1.98, and 2.00 eV for 300 °C, 500 °C, and 800 °C heat-treated samples respectively as shown in Fig. 4b–d. The bandgap values of hematite, maghemite, and magnetite found in this work are in good agreement with previous works [49].

Fig. 4 UV-Vis diffuse reflectance spectra (a) and $[F(R)hv]^2$ versus $h\nu$ plot of electro-coagulated sludge thermally annealed at 300 °C (b), 500 °C (c), and 800 °C (d)

Fig. 5 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of raw electro-coagulated sludge

3.5 Thermogravimetric analysis

The thermogravimetric analysis (TGA) versus differential thermal analysis (DTA) for purified through beneficiation electro-coagulated sludge was determined as shown in Fig. 5. The surface and absorbed water removal was observed from the TGA curves approximately up to 99.7, and extend to 248 °C, respectively. This accounts for 0.78 mg weight losses. Correspondingly, the endothermic peak has occurred around 99.7 °C which is a result of evaporation of the bonded water molecules from the EC sludge. A dramatic weight loss, around 0.92 mg, was observed from 250 to 580 °C suggests that the dehydroxylation processes. The results indicated that high weight loss occurred in two steps, the first at around up to 248 °C. The second weight loss up to 580 °C, is associated with

Fig. 6 Zeta potential versus pH ionic activity of solution for raw and thermally treated (100–800 °C) EC sludge

the structural hydroxyl content ($-\text{OH}$) [50, 51]. The differential thermal analysis (DTA) shown that the sharp exothermic peak around 317 °C which is the result of the oxidative transformation of Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$; expected in the temperature range of 200–400 °C [52]. Also, the small exothermic peak around 507 °C accounts for the phase transformation from $\gamma\text{-Fe}_2\text{O}_3$ to $\alpha\text{-Fe}_2\text{O}_3$. Differential thermal analysis (DTA) results are associated with the mass loss of water, organic contaminant, and structural $-\text{OH}$ as in the TGA and also with phase transformation [41]. It can be deduced that it by varying the temperature different form of iron oxides can be produced. With increasing temperature, the oxidative transformation favors magnetite/maghemite toward hematite formation. The total weight loss of raw electro-coagulated sludge determined by thermogravimetric analysis (TGA) in the temperature range of 99.7–580 °C was 1.7 mg out of 15 mg which is 11.33% losses. From this much of losses, it can be deduced that decomposable organic pollutants from the sludge are insignificant suggesting the iron hydroxide and oxy-hydroxide flocs have been produced during the electro-coagulation treatment process.

3.6 Zeta potentials

The nanostructure materials having a magnetic nature can affect the interfacial electrical characteristics for different uses; such as photocatalytic application at the solid–liquid electrolyte interface, and the surface electric charge. Thus, electrophoretic mobility can be assessed by electrokinetic measurements [53]. The electrokinetic behavior of electro-coagulated sludge in acidic and basic solution was investigated and the zeta potential was examined. As shown in Fig. 6 zeta potential–pH curve for the raw and thermally

treated (100, 300, 500, and 800 °C) EC sludge with a range of solution pH. The point of zero charges occurs at a pH of 10 and a range of zeta potentials was recorded with -42 to 39 mV. These results indicate that the material may agglomerate and have an excellent adsorptive feature [54].

As the pH increase, raw and thermally treated EC sludge expected to have more hydroxyl groups charged surface which favors the more positive zeta potential values. Thermally treated EC sludge has high zeta potential value as compared with the raw EC sludge. The highest zeta potential is achieved in a thermally treated EC sludge at 800 °C due to the raw EC sludge has different impurities from the textile effluent which can shield the electrostatic interaction. Also, the maghemite and hematite nanoparticles have not existed before thermal treatments. This is also confirmed with XRD diffraction patterns and SEM micrographs.

4 Conclusion

The wet textile factory is treating its effluent with electro-coagulation process but the amount of sludge produced by wastewater treatment plants is increased and its accumulation is a burden to the factory. This can affect the environment adversely and the need for effective reuse of the sludge becomes a vital issue in the world. Thus, the study reports a promising way of recycling mechanisms of sludge into valuable iron oxides which can be used for industrial, commercial, and medical purposes. Materials characterization by XRD suggests that iron oxide nanoparticles are contained dominantly and its microstructure was observed. FTIR and XRD confirmed that iron hydroxide disappeared after heat treatment which tells that transformation of iron hydroxide to maghemite and hematite have occurred. It can be deduced that iron oxide nanoparticles can be recycled from wastewater sludge having electrochemical processes in their effluent treatment plant for different applications, such as for water and wastewater treatment, for printing machine industrial and medical uses. Utilizations of sludge from the electrochemical processes of wastewater treatment are a good opportunity for different commercial and industrial applications as well as waste management for a sustainable environment. Also, this research findings can have a potential to industrialists and environmentalists to think over in such a way that controlled sludge recycling mechanisms during wastewater treatment is beneficial in terms of cost and sustainability. Furthermore, an integrated wastewater treatment system with resource recycling technology at the initial stage of the installation becomes an important issue to consider.

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Compliance with ethical standards

Conflict of interest The author declares that they have no known competing for financial interests or personal relationships that could have appeared to influence the work reported in this work.

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