Recycling of a wastewater to iron oxide micro structures

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Keywords: wastewater recycling, iron oxide powder, electrochemistry, SEM-EDX, XRD analysis

Abstract

The proposed work describes new perspectives for recycling of a salty industrial wastewater to micro-structured iron oxides with257 potential for minor carbon- and metallic contaminations. By-products generated by electrochemical treatment of a rubber wastewater with sacrificial steel anode were separated, dried, desalinated, and thermally processed at 800 and 1100 °C in a nitrogen atmosphere to investigate the effects of chemically bound oxygen on iron oxide formation. The obtained powder products were different phases of iron oxides, such as hematite, maghemite, magnetite; depending on the annealing temperature. All of the phases are interesting from a recycling point of view, the microstructure, elementary composition and crystallinity of the solid products before and after thermal treatment were investigated via SEM-EDX and PXRD techniques.

Introduction

The primary interphase by-products of wastewater electrochemistry induced by iron/steel electrodes are mainly ferrous hydroxide Fe(OH)2 (aka ‘green rust’) and ferric hydroxide Fe(OH)3. Iron hydroxide generation induces electrophoretic grouping of negatively charged colloids in the vicinity of a positively charged electrode, i.e. the anode, followed by a formation of polyatomic surface complexes between Fe(II), Fe(III) cations and colloidal anions [1-4]. In other words, the active functional groups of hydrocarbon chains (HC) are physically adsorbed to Fe(OH)3 flocs by weaker Van der Waals forces and removal of organic contaminant is a Fe(OH)3-driven electrostatic reaction with adsorption of hydrocarbons to hydroxide surfaces to form (HC-Fe(OH)3) coagulates [5].

Other dissolved organic and inorganic compounds or metal cations also contribute to the electrococagulation mechanism, therefore even heavy metal or alkali content in wastewater can be hydrolyzed, oxidized and coagulated through complex electrochemical mechanisms. The boundary conditions of Fe (II-III) cation and hydroxides formation with their dependencies on pH is clearly depicted in the so-called Pourbaix diagram which shows operational regimes/regions of Fe anode [2, 7]. Beside pure hydroxides, oxyhydroxides can also be formed and removed like goethite α-FeOOH and lepidocrocite γ-FeOOH [6, 8].

Dehydration of coagulated complexes based on iron hydroxides or/and oxyhydroxides is followed by iron oxide formation [6, 8]. High temperature dehydration and oxidation of iron oxides, hydroxides are followed by several temperature-dependent phase interchanges between phases hematite-maghemite-magnetite [9-13].

In oxygen-rich atmosphere, magnetite usually goes through several temperature-dependent stages during rapid oxidation leading to stable hematite (α-Fe2O3) formation:

1. 4 Fe2O3 + O2 → 6 γ-Fe2O3; in temperature range 200 °C - 400 °C.
2. γ-Fe2O3 → α-Fe2O3; starting at about 375 °C and terminating between 525 and 550 °C. This transition temperature is related to the temperature of formation of the γ-Fe2O3.
3. 4 Fe2O3 + O2 → 6 α-Fe2O3; starting from 550 °C. The culmination and point of completion of this reaction are dependent upon the extent of reaction 1.)
It can be concluded that increasing temperature favours the oxidative magnetite/maghemite transformation toward hematite formation.

Iron oxides have broad utilization in the printing technology, since pigments manufactured of hematite are red, those made of magnetite are black and maghemite-like pigments are brownish[14, 15]. Magnetic iron oxide particles (magnetite Fe₃O₄ and maghemite γ-Fe₂O₃) have numerous applications in industry and medicine as catalysts, ferrofluids, magnetic inks/seals and recording media [16], contrast agent in MRI analysis or as injected bio-agent in hyperthermia-based cancer treatment [17]. Hematite (α-Fe₂O₃) enriches the group of promising materials dedicated for photocatalysis due to its stability in acidic environments and low manufacturing costs [18–20], but its application is also recognized in water splitting, gas sensors and photovoltaics [21].

Moreover, iron oxides deliver promising results in water decontamination. The influence of iron oxide nanoparticles on the adsorption of organic matter on magnetic powdered activated carbon was investigated by Lompe et al. [22], where authors highlighted the synergy of activated carbon and iron nanoparticles to produce adsorbents for natural organic contaminants. Synthesis and properties of a high-capacity iron oxide adsorbent for fluoride removal from drinking water is in detail described by Zhang et al. [23]. Fe₃O₄ nanomaterials and their effect on wastewater treatment were investigated in several studies. Tamjidi et al [24] investigated Cr(III) removal from aqueous solution by modified CaO/Fe₃O₄ nanocomposite. The best removal efficiency was achieved by altering various parameters such as temperature, pH, or contact time. Ahmadi et al [25] used bentonite/Fe₃O₄ nanocomposite synthesized by a chemical coprecipitation method. The chemical properties of the bentonite/magnetite nanomaterials were studied by x-ray diffraction, scanning electron microscopy, and Fourier-transform infrared spectroscopy. The obtained material was used for the removal of Cd(II), Pb(II), and Ni(II) ions from aqueous solutions. Further utilization of iron oxide nanomaterials for wastewater treatment is presented by Mousavi et al [26]. Fe₃O₄ nanoparticles were modified by oak shell and their removal of Ni(II) was investigated. Chemical and physical properties of the adsorbents were studied using FTIR, SEM, and TEM. The efficiency of graphene oxide/Fe₃O₄ nanoparticles and Kombucha Scoby and their efficiency for Pb(II) removal was also studied by Mousavi et al [27]. Similarly, to the previous work, the structure of the nanomaterials was investigated via FTIR and SEM.

The aim of this paper is to study the synthesis of salt-carbon-iron hydroxide adsorbed complexes during electrochemical treatment of an industrial wastewater and the formation of salt/iron oxide composites by their subsequent thermal processing in nitrogen atmosphere.

**Experimental setup and method**

Electrochemical treatment of an industrial wastewater (rubber industry) was performed in a PTFE-insulated coaxial flow-through electrochemical reactor, comprising of a central steel anode and an outer cylindrical cathode made of steel having an anode-to-cathode surface ratio of 5:7 and annular electrode gap of 1 cm. The geometry of the holes of inlet and outlet ensured the uniform fluid flow through the reactor chamber and flushing of formed gases and solids. Prior to the electrochemical treatment, the wastewater was filtered to remove coarse particulates. That was followed by the measurement of chemical oxygen demand (COD) and ammonia nitrogen content of the wastewater sample to form a conductive electrolytic environment and enhance electro-oxidation processes. During the wastewater treatment 5 liters of wastewater were continuously recirculated by a chemical membrane pump at constant flowrate of 3 l min⁻¹, which equaled to 2.65 cm s⁻¹ flow velocity through the electrochemical reactor. The electrochemical reactor was operated in galvanostatic mode at 156 mA cm⁻² current density for 1 h of total treatment time.

After the treatment, the generated iron-rich sludge was collected from the treated wastewater sample and agedotopically dehydrated for subsequent thermal processing. Next, the anhydrous product was sampled to a porcelain cup and placed inside the pyrolysis chamber. Nitrogen flow at 10 l min⁻¹ was introduced for 15 min to establish an inert atmosphere, then the sample was thermally treated under steady nitrogen flow at 11 l min⁻¹ with 7 °C min⁻¹ heating rate and 2 h of isothermal dwell at the temperatures 800 °C and 1100 °C respectively. Elemental carbon content of the dehydrated sludge and thermally treated sludge was determined by a Thermo Finnigan Flash EA 1112 analyser. The samples after thermal processing were desalinated in distilled water at 60 °C to dissolve and eliminate NaCl content from the metal oxide matrix.

Morphology of the dehydrated, pyrolyzed and desalinated samples and localized elemental composition was determined by SEM-EDX (HITACHI TM3030). EDX quantitative elemental composition analysis was provided through the use of BSD (Backscattered Diffraction) full detector with 15 kV-image mode. The presence of crystalline phases in the dehydrated and pyrolysed sample were clarified by qualitative x-ray diffraction analysis using program Match! with included crystallographic database. The powder x-ray diffraction (XRD) patterns were collected using a Brag-Brentano parafocusing automatic powder diffractometer Philips PW1820 equipped...
with x-ray tube providing Co Kα radiation (0.179 0300 nm), curved graphite monochromator placed in the diffracted beam and automatic divergent slit. The experimental conditions were as follow: exciting voltage: 40 kV, anode current: 30 mA, a step size of 0.02° and a counting time 1 s per step and measuring over the 2θ range of 3°–90°. Samples were slightly ground using an agate pestle with mortar prior, filled into a flat silicon zero-background sample holder, measured and stored at room temperature.

Experimental results and discussion

As mentioned before, the wastewater was mechanically prefiltered from particles to avoid any obstruction within hydraulic set-up and interference of large particulates with the investigated NaCl-metal oxide matrix. Thus, the filtered wastewater had a residual COD 200 ± 50 mg l⁻¹ and pH 7.6. The addition of NaCl provided 18 mS cm⁻¹ electrical conductivity allowing energy effective electrochemical extraction of organics into an iron-rich sludge. Since solved NaCl is widely used for setting pH and electrical conductivity of wastewater during electrochemical treatment, Na⁺ and Cl⁻ ions follow their own reaction pathways in formation of hypochlorous acid HOCl and its ClO⁻ anion. These species have good oxidative potential and ability to remove pollutants through an electrocoagulation mechanism [5]. Moreover, these chlorine-based species serve as an additional source of oxygen in iron oxide synthesis in inert nitrogen atmospheres.

Amorphous iron hydroxides and extracted hydrocarbon structures were found to be the main fractions of the sludge, which is in good agreement with other studies [1–5]. In terms of elementary analysis of the sampled and subsequently dehydrated salty sludge, its carbon content was estimated at 4.5 w%. This confirms efficiency of electrochemical wastewater decontamination (COD measurement of treated wastewater sample was not possible due to high Cl concentration). SEM-EDX observations (figures 1–4) confirmed the local presence of C, N,Fe,O,Na,Cl and Si. The detection of F can be linked to the electrochemical erosion of reactor insulation, while the traces of Cr and Ni might come from the treated wastewater. Qualitative and semiquantitative powder x-ray diffraction analysis showed only the presence of halite (NaCl) and minor amount of quartz (SiO₂) and sodium chlorate (NaClO₃) crystallites. Morphology analysis showed a quasi-homogeneously distributed circle-like NaCl-based complexes surrounded by amorphous matrix that is mainly containing iron, oxygen and carbon according to EDX analysis.
Figure 2. SEM image and elementary analysis of an extracted sludge after thermal treatment at 800 °C in nitrogen atmosphere.

Figure 3. SEM image and elementary analysis of desalinated thermally treated sludge 1100 °C in nitrogen atmosphere.
The thermal treatment of dehydrated sludge carried out in nitrogen atmosphere at temperatures of 800 °C and 1100 °C resulted in a significant structural transformation (figures 1–4) and oxidation of the sample followed by crystallization of several constituents. Figures 1–2 and 3–4 show the morphology of treated sludge by-product before and after desalination, respectively. It can be seen, that removing of halite content from the matrix resulted in more homogenous morphology of synthetized iron oxide microstructures. One must note that due to the presence of inert atmosphere the oxidation could have been taken place exclusively due to the presence of bonded oxygen and not via externally induced oxidation. First step in iron oxide formation is a dehydration of amorphous iron hydroxides and oxyhydroxides [9, 28] even at low temperature regions where the formation of hematite, magnetite and maghemite were also registered.

Beside the halite content, surprisingly, both hematite and maghemite were found to be the most abundant iron oxides. Magnetite occurred only at minor concentrations. One could therefore expect an almost pure \( \alpha \)-Fe\(_2\)O\(_3\) formation after a high temperature heat treatment in our experiment. However, the main observed crystalline products with a descending abundance were halite > hematite > maghemite > magnetite at 1100 °C (figure 6) and halite > hematite > maghemite at 800 °C (figure 5).

As it is described in the above-mentioned references, magnetite is first transformed to maghemite, then the increase of temperature induces total transformation into stable hematite in oxygen-rich environment. In case of larger micro-particles or bulk material, oxidation proceeds in a strongly time and temperature dependent manner; the maghemite can therefore be present together with small amount of yet non-oxidized magnetite and maghemite within a bulk oxide [13, 29]. In our study, however, the unexpected significant abundance of maghemite can be assigned to the unavailability of free oxygen causing incomplete magnetite-to-hematite transition in the high temperature region, where the sample was kept for the longest time. This is well supported by work of Kahani [30], who showed a novel pathway diagram for formation of magnetite from iron oxyhydroxides and iron oxide as dependence of pH and temperature.

The SEM-EDX analysis detected small amounts of carbonized content in thermally treated samples, whose morphology could not be clarified yet. PXRD analysis did not show any crystalline carbon structures after heat treatment. By thermal treatment the elementary carbon content captured via electrocoagulation decreased below detection limits of our analyser, signaling degradation to simpler volatile hydrocarbons and also oxidative consumption of bonded oxygen. The peaks at 28.5°, 39°, 47°, 48.5°, 58.5°, and 77° are the main peaks related to the hematite phase with the additional peaks at 42°, 52°, 64.5°, 68°, 74°, and 79° are overlapping with

Figure 4. SEM image and elementary analysis of desalinated thermally treated sludge 800 °C in nitrogen atmosphere.
the peaks of maghemite and magnetite phase. The main peaks of halite are at 32°, 37.5°, 53°, 64.5°, 67.5°, and 79°. Since the sample is a mixture of various phases no further analysis such as Rietveld analysis and weight ratio of the present phases was performed.

One must note that phase transition of iron oxides is also size-dependent. In case of nanoparticles with d < 20 nm, the maghemite phase is usually the most stable phase due to the dominant surface energy term which is lower than in case of hematite. Transformation to hematite requires therefore higher temperatures for nanomaterials than for a bulk material. According to Krispin [31], maghemite particles of sizes < 10 nm annealed at 700 °C (in air) can be kept without phase change for several hours. In case of phase change, the particle size increases rapidly to > 30 nm [31]. Such phenomenon is well registered in our observations since samples were kept much longer in temperature range of reaction (3) than in temperature range of (1) and (2). But nevertheless, phase transition rather continued in the way of maghemite formation and magnetite reduction in treatment at 1100 °C and temperature decrease down to 800 °C resulted in complete transformation of magnetite into hematite and maghemite according to PXRD (figure 5).

Dissolving of halite content from thermally processed products in distilled water resulted in a salt-free iron oxide confirmed by SEM-EDX analysis (figures 3 and 4). As an example of its further utilization potential, the sample processed at 800 °C can be regarded as a low-cost Fe₂O₃ pigment with brownish red colour, that was made by a waste-to-oxide process utilizing chemically bound oxygen from water. Another attractive application to be considered is a direct reuse of these iron oxides in the treatment of wastewater streams. The process of obtaining various iron oxides or iron oxide composite structures of defined qualities could be refined for the application of choice.

Conclusion

This paper presents a novel way of wastewater recycling and its transformation into valuable iron oxides of an industrial importance. Salted wastewater samples taken from rubber manufacturing procedures have been electrochemically treated in the presence of the controlled dosage of Fe ions. The pollution content from wastewater coagulated in form of iron hydroxide bulk has been collected and thermally treated at temperatures
800 and 1100 °C in nitrogen atmosphere to avoid the influence of external oxygen. The synthetized powder products were different phases of iron oxides, namely: maghemite, hematite at 800 °C and hematite, magnetite, maghemite at 1100 °C. By removing the initial salt content, the relatively pure mix of iron oxides with pigment features was obtained. The further utilization of the obtained materials for wastewater treatment may lead to significant cost reduction. This observation has a potential to open new horizons for a more controlled wastewater recycling, and cleaner maghemite-hematite formation in form of microstructures within a transformed waste matrix.

Acknowledgments

The author(s) would like to acknowledge the contribution of the COST Action CA15107, foundations Bethlen Gabor Alap and Baross Gabor Alap. The research activities were partially supported by the Ministry of Economy of Slovak Republic within the grant scheme Innovation Vouchers 2018.

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Figure 6. The results of a qualitative phase analysis of a dehydrated sample processed at 800 °C.
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