Use of Fe and Al Containing Electrocoagulation Sludge as an Adsorbent and a Catalyst in Water Treatment

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ABSTRACT

In this study, three different electrocoagulation (EC) sludges were studied as an adsorbent (removal of humic acids) and as a catalyst (catalytic wet peroxide oxidation, CWPO, of bisphenol A (BPA). The sludges originated from electrocoagulation process in which aluminum (Al) and iron (Fe) electrodes were used for the treatment of mining industry wastewater. All the materials were used as dried sludge and as calcined material. The stability of these materials was studied in neutral and alkaline conditions with analysis of the leached iron content in solution.

Based on the EC sludge characterization with X-ray fluorescence (XRF), X-ray diffractometer (XRD) and diffuse-reflectance infrared Fourier transform spectroscopy (DRIFT) different forms of Fe occurring in EC sludges were found. The Brunauer–Emmett–Teller (BET) method showed reduced surface area after calcination process. Stability of the sludges was studied in neutral conditions, and the amount of iron leaching was low (<1.4 ppm). Adsorption experiments showed that the removal of humic acids (measured as TOC) was over 50 % in all tested materials in the pH range of 3 – 9, and over 92 % with the S3 calcined material in all studied pH range. The calcined samples were catalytically more active than raw material in CWPO of BPA. The highest removal of BPA was 85 % over calcined sludge. Therefore, calcined EC sludges are suitable materials for catalyst and adsorbent use.

Main novelty of this paper was the finding of sludge modification in the EC process of water treatment through different electrode material and current density. This modification can be made in EC water treatment process, and it may provide low-cost materials to different utilization of EC sludge.

KEYWORDS

Electrocoagulation, sludge, utilization, circular economy, extraction, adsorbent, catalyst

INTRODUCTION

Many countries and Unions have made their own regulations to circular economy. Main goals of these regulations are to reduce the usage of natural resources, produce less waste and make more sustainable products. Some areas, like European Union (EU), has also stated this to be an economically important area and will create more employments and sustainable economic growth to area. EU has made circular economy action plans (CEAP) (First Circular economy plan, Circular economy action plan) to make more environmentally safe products and save natural resources. The present action plan (Circular economy action plan) is affecting in chemicals, industry, plastics, waste, and recycling. In all these areas regulations are tighten recently. EU has stated in present action plan that they want to lead the way to circular economy in a global level and help also developing countries to benefit these results. EU has stated in Lissabon Treaty in 2007 that environment is one of the key areas in EU area. In 2018 and 2019 European Parliament and the Council set several different Directives (e.g., Waste framework, Landfill, Packing and Packing waste Directives) that have regulations to waste and its management. The Waste Framework Directive sets concepts and definitions to different waste and recycling. There is also stated the reuse and recycling policy in EU area. The efficient use of resources is also considered to make savings in economics and reduce greenhouse gases while creating a new industry areas and employments. The Landfill Directive is affecting heavily to the industry and to fill these needs, all the side streams reuse purposes are needed to study before landfilling any material. In this Directive economic and environmental aspects are in important role. EU is not the only area that have environmental regulations (National Environmental Protection Act, US; Environmental Protection and Biodiversity Conservation act, Australia, Canadian Environmental Protection Act).

Water treatment is important to provide drinkable water and reduce the amount of harmful substances in waterbodies. Electrocoagulation (EC) is one water treatment technology which was invented in the late 19th century (Elmore, 1904). There are several different chemical techniques involving in EC systems like coagulation, oxidation, flotation, and sedimentation. There is an anodic reaction in EC that dissolves metal to the water with help of electricity. The dissolved metal, mainly in easily reactive M^{2+} or M^{3+}, which reacts with impurities and forms sludge. In cathode water

molecules are brake up to hydrogen (H_2^+) and hydroxide (OH^-). (Holt et al., 2002). In the EC system some sludge is formed to the top of the water or settles to bottom of the reactor. The amount of forming sludge in EC is less than in conventional chemical precipitation (CP) process and consists metallic oxide/hydroxide. It is also easy to dewater, settles easily, is acid resistant and stable (Mollah et al., 2001; Shin et al., 2006). The sludge is formed in batch or continuous EC process. Both processes have a reactor chamber, a power source, and electrodes in their simples' forms. In batch EC a stirrer is usually used to make water move in reactor and electrodes are hanging in most cases. In continuous EC the flow of water acts similar way than stirrer in batch EC and electrodes can be fixed. The EC system have various numbers of electrode pairs and it is not limited in any ways. (Chen, 2004; Sahu et al., 2014; Rajaniemi et al., 2019).

EC process produces sludge which is not currently efficiently utilized. Depending on electrode material, sludge is usable in different ways as building material, adsorbent, catalyst, pigment, etc. (Rajaniemi et al, 2021a). There are studies of EC sludge in fertilizer use (Rajaniemi et al 2021b, Kruk et al., 2014). These studies have made with magnesium electrodes and with water that has phosphate and nitrogen content. Iron oxides are used as pigments and EC sludge that has iron oxides can be used as pigment according to Tezcan et al (2017). The EC sludges has some properties that are suitable for non-structural building material use (Adyel et al., 2013; Sharma et al., 2016). Some individual EC sludge studies for suitability for anaerobic digestion during municipal wastewater treatment (Huthan et al. 2006), in ultrasound-mediated Cr(VI) reduction (Kathiravan et al., 2011) and nanocrystalline source material (Li et al., 2013). Commonly used catalysts are iron oxide-based catalysts in various applications. EC sludge can be used as catalyst in different applications like catalyst for peroxymonosulphate activation (Ghanbari et al., 2020) or photocatalyst (Shon et al., 2010). The iron oxide-based adsorbents are also widely studied, and EC sludge has used as adsorbent in some applications like dye (Golder et al., 2006) and fluoride (Yilmaz et al., 2015) removal. It is important to find multiple usage to one sludge to make it more reusable. Iron and aluminum containing sludges were studied in this work, and the potential utilization applications were tested as an adsorbent and catalyst.

The objective of this study is to investigate three different EC sludge materials with raw and calcined versions and their suitability to different utilization applications. The sludge contained iron oxides, which is widely used as adsorbent and catalyst. The chemical composition of sludges was determined for all EC sludges from same source produced with different electrodes. The main utilization applications chosen to this study were the use of EC sludges as an adsorbent for humic acid removal and the use as a catalyst in catalytic wet peroxide oxidation (CWPO) for bisphenol A (BPA) removal. In adsorption experiments, the removal % of total organic carbon (TOC) was determined before and after the adsorption, where humic acid was removed from aqueous solution. In the catalytic experiments, the removal of BPA was measured as a function of treatment time. Solubility of the materials was tested in both neutral (water) and acidic (sulfuric acid) conditions to

find out the stability of the sludges. Based on our knowledge, there are no studies presented in the literature in which two kinds of utilization applications of the three different types of sludges have been screened for water treatment.

MATERIALS AND METHODS

Electrocoagulation sludge

Electrocoagulation sludge's properties are strongly depending on electrode material and used current density in the process. Sludge properties are slightly affected from treated water and sludge is more compact than in other treatment methods like chemical precipitation (CP). (Mollah et al., 2001; Sahu et al., 2014). All the three sludges used in this study was collected from continuous EC processes, that is based on patent FI20165317 (Rajaniemi et al. 2016)

Sludges from mining industry wastewater treatment pilot plant (MIWTPP) were collected from continuous EC equipment that has maximum treatment capacity of 1.5 m^3 per hour. This EC water treatment equipment is in Oulu Mining School pilot process with closed water treatment cycle. Several kinds of mainly metal containing mining waters varied inside of periods of each sludge collection period. The S1 was collected using both Al and Fe sacrificial anodes. The S2 was collected from several different process using mainly Al sacrificial anodes with iron electrodes in the last phase. The S3 had several different process test sludges using mainly Fe sacrificial electrodes. This continuous EC process used five electrode pairs that had treatment area of 0.2 m^2. The current density in this process was 40 A/m^2 and used flow has been about 0.9 m^3 / h.

Characterization of materials

The sludge from EC equipment was collected from overflow and dried at 105 °C. After drying sludge was crushed and grinded. The sludge analysis in thermogravimetric analysis (Netzsch STA 409PC/PG) were defined up to 1000 °C and based on this 550 °C was chosen as calcination temperature, because after that the temperature the change of TG value was almost stable. Some amount of all sludges was calcined at 550 °C for four hours with temperature raise of 1 °C per minute and 2 h stabilization at temperature of 360 °C. All sludges' chemical compositions were analysed with X-ray fluorescence (XRF, PanAnalytical Minipal 4) analysis.

The phase composition of EC sludges was analysed by X-ray diffractometer (XRD, PANalytical X'pert Pro X-ray diffractometer) using monochromatic CuKα1 radiation (λ=1.5406 Å) at 45 kV and 40 mA. The diffractograms were collected in the 2θ range 6−90° at 0.017° intervals and with scan step time of 100 s. The crystalline phases and structures were analysed by HighScore Plus software using the Powder Diffraction File standards from the International Centre for Diffraction DATA ICDD (PDF-4+ 2020 RDB). Diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) was

used to analyse functional groups on the surface of EC sludges. DRIFT spectra were recorded on a Bruker PMA 50 Vertex 80 V (Bruker, Billerica, MA, United States), equipped with a Harrick Praying Mantis diffuse reflection accessory and a high-temperature reaction chamber, by baseline measurement using KBr. Measurements were performed at 400–4000 cm^{-1} with a resolution of 4 cm^{-1} and 500 scans per minute.

Specific surface area (SSA), pore volume (PV) and pore size distribution (PSD) of the samples, were determined at 77.15 K with Micromeritics 3 Flex physisorption instrument (Micromeritics Instruments, Norcross, GA, USA). Exact portions of each sample (100–200 mg) were degassed with Micromeritics smart VacPrep gas adsorption sample preparation device at pressure of 0.67 kPa and at a temperature of 413 K for 3 h to remove impurities. Adsorption isotherms were measured in liquid nitrogen (77.15 K) at constant temperature. Data was processed with 3Flex version 5.02 software. SSAs were calculated from adsorption isotherms based on the Brunauer–Emmett–Teller (BET) method (Brunauer et al., 1938). The model selected to estimate the PSD and PV of the sample materials was density functional theory (DFT) based on a model of independent slit-shaped pores. The pore size distribution was calculated from the individual volumes of micropores, mesopores, and macropores with the DFT model. By using the instrumental setup, micropores down to a diameter of 0.35 nm can be measured. A previous study has reported that SSAs are typically measured with a precision of 5% (Hacley and Stefaniak, 2013).

Stability tests in neutral and acidic conditions

Solubility of the materials were tested in both neutral (water) and acidic (sulfuric acid) conditions. In water leaching test 2.5 g of each sludge was mixed to MilliQ water solution. In acidic leaching experiment solution was made with Milli-Q water and commercial H_2SO_4 (95 wt-%, J.T. Baker). The amount of H_2SO_4 was defined to be 1.77 mL / L at pH 1.5. All the samples were mixed for 24 h with 300 rpm and filtered through 0.45 µm filter paper. The iron content of the filtered samples was determined with AAS. All the experiments were duplicated. The pH was measured using Hach HQ30d pH electrode.

Under the acidic conditions, the amount of Fe_2O_3 in pH 1.5 was determined to be 1.77 g / L from following reaction 1:

$$Fe_2O_3 + 3\ H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3\ H_2O \qquad \text{Reaction 1}$$

Each different sample had different value of Fe_2O_3. In Table 1 is presented the calculated amount of sample for each sample. Fe_2O_3 concentration was defined from elemental analysis of XRF with following equation

$$Amount\ of\ Fe_2O_3 = \frac{wanted\ amount\ of\ Fe_2O_3\ 1.77\ g/L}{Fe_2O_3\ \%\ in\ XRF\ analysis} \qquad \text{Equation 1}$$

where amount of Fe (g / L) is calculated dividing the wanted amount of Fe_2O_3, 1.77 g / L, by wt-% of Fe_2O_3 determined with XRF elemental analysis.

The iron content, in all experiments, was analyzed with in ICP-OES analysis (Thermo Electron iCAP 6500 Duo, Thermo Fisher Scientific, Waltham, MA, USA). Leaching of the materials was evaluated by using water extraction and acid extraction by mixing materials in the laboratory shaker for 24 h, filtered through 0.45 µm filter paper. After mixing and filtering the Fe concentration was analyzed by AAS. All the experiments were done in duplicate.

Use of electrocoagulation sludge as a catalyst in catalytic wet peroxide oxidation

All the sample materials were dried, crushed and grinded and finally sieved between 63 – 150 µm particle size. The catalytic wet peroxide oxidation (CWPO) experiments were done to study EC sludge as iron catalyst in the aqueous oxidation of BPA solution. The initial concentration of BPA in the solution was 60 mg / L. The hydrogen peroxide (H_2O_2) concentration in solution was determined to be 0.15 w-%. Three-necked 500 mL round bottom flask was used in the oxidation reaction with the magnetic stirrer. The concentration of catalyst in each different experiment was 4 g/L and added to reactor. 160 mL of BPA solution was added to flask under continuous stirring. The temperature was adjusted at 50 °C and the reaction time was 3 h. Initial sample was collected when solution reached 50 °C. Every 30 min 10 mL sample was taken. and 10 mL of H_2O_2 solution was added. Last addition was made at t = 120 min. All the samples were filtered through 0.45 µm filter paper. The pH and dissolved oxygen content were taken during experiment when sample was collected, and BPA concentration was measured in HPLC from samples. All the experiments were duplicated.

Electrocoagulation sludge as an adsorbent in humic acid removal

Synthetic humic acid solution was prepared by using commercial humic acid sodium salt (Sigma-Aldrich, technical grade 50 – 60 %) and it was used in adsorption tests. The initial humic acid concentration during experiments was 23 mg / L and 1 g of each different adsorbent, calcined and non-calcined of each sludge (S1, S2 and S3), was added to 250 mL of humic acid solution. A magnetic stirrer was used at 250 rpm for 30 min. All the materials were tested in four different pH values: 3, 5, 7, and 9 at room temperature (22 ± 2 °C). The pH was controlled continuously during the 30 min treatment time with 0.1M NaOH or HCl addition. After the 30 min treatment time, samples were filtered through a 0.45 µm filtration paper and the rest humic acid concentration was analysed with TOC. Iron leaching during adsorption experiments was studied and therefore, iron concentration of each sample was measured by AAS. The TOC analysis was performed using a Skalar FormacsHT Total Organic Carbon/total nitrogen analyzer (Breda, The Netherlands). All the experiments were done as duplicate.

RESULTS AND DISCUSSION

Characterization of materials

In Table 2 is shown the composition of EC sludges determined by XRF. The presented 10 oxides are covering over 97 % of S1 and S1 calcined samples, over 98 % of S2 and S2 calcined and over 99 % of S3 and S3 calcined.

The amount of Fe_2O_3 varies from 45.9 % to 67.9 %, Al_2O_3 from 5.97 % to 15.25 % and SiO_3 1,98 % to 17.48 %. In all samples the combined oxides % of Fe_2O_3, Al_2O_3 and SiO_3 were between 72 – 80% while the ratio of Fe_2O_3, Al_2O_3 and SiO_3 were in S1 and S1 calcined about 9:1:3, S2 and S2 calcined 4:1.25:1 and S3 and S3 calcined 30:5.5:1, respectively. The ratio of Fe_2O_3 : Al_2O_3 were 9:1 in S1 and S1 calcined, 4:1 in S2 and S2 calcined and 8:1 in S3 and S3 calcined and total content of Fe_2O_3 : Al_2O_3 were in S1 and S1 calcined approximately 58.9 %, S2 and S2 calcined 61.5 % and with S3 and S3 calcined 77.8 % of total elemental content.

The used electrode correlates to the sludge content. From Table 2 can be determined that the amount of Fe_2O_3 increases and aluminum have not significant changes with S1 between raw and calcinated sample and with other sludges amount of Fe_2O_5 decreases and amount of Al_2O_3 increases. There are only minor changes in SiO_3 content in each sludge after calcination. The change in other elements before and after calcination are insignificant.

DRIFT spectra of both untreated (S1-S3) and calcined (S1 calcined-S3 calcined) EC sludges are shown in Figure 1. All samples exhibited broad peak at ~ 3400 cm^{-1} which is characteristic to the O–H stretching in O–H groups (Sobhanardakani et al., 2018). and the peak at 1650 cm^{-1} corresponded to the H–OH stretching vibrations of absorbed water (Mao et al., 2009). Furthermore, the peak at around 1530 cm^{-1} related to NO_2 antisymmetric stretching (Liu and Wu., 2019) which intensity has decreased in S1 calcined, S2 calcined and S3 calcined due to the heat treatment of those samples. All EC sludges presented several peaks related to the iron. The peaks observed in the wavenumber region 580-630 cm^{-1} can be attributed to the stretching vibration mode to the Fe–O bonds in the Fe_3O_4 (Nalbandian et al., 2016). Moreover, characteristic peak of the bending vibration mode of Fe_2O_3 can be seen in samples S2, S2 calcined and S3 at wavenumber 555 cm^{-1} (Sobhanardakani et al., 2018). According to Sobhanardakani et al. (2018) the bending IR vibration of Fe_2O_3 should exhibit at 446 cm^{-1} and in samples S1, S1 calcined, S2 and S2 calcined peaks can be seen in this wavenumber area. However, SiO_2 has also IR vibrations in this area namely at 435-483 cm^{-1} which correspond to the Si–O–Si and O–Si–O bending vibrations (Yunsheng et al., 2007). According to XRD (Figure 2), both phases are present in all samples, but the overlapping of vibrations hinders partly of both peaks. Moreover, the asymmetric and symmetric stretching mode of SiO_2 can be observed at 1100 and 808 cm^{-1} (Nhan et al., 2013) especially in non-calcined samples. In addition to iron oxides, EC sludges contained around 10 wt.% SO_3 (Table 1). The XRD results showed the

presence of FeS_2 (Figure 2) and the peaks related to the stretching of S–S and Fe–S can be seen in the DRIFT spectra at wavenumber region 607-622 cm^{-1} (Siavash et al., 2015) in calcinated samples.

XRD patterns of the S1, S1 calcined, S2 and S2 calcined showed high peaks of SiO_2 (ICDD 01-077-8621). In the sludges S1 calcined and S2 calcined Fe_2O_3 (ICDD 01-084-2782) peaks were found while S1 and S2 iron was in form of FeS_2 (ICDD 04-002-1587). S3 calcined sample had clear peaks of Fe_2O_3 and $CaSO_4$ (ICDD 04-008-2186) while SiO_2 was not clearly in presence. In S1 and S2 had also peaks from $CaSO_4$. Gypsum (ICDD 04-015-4421) occurred in untreated sludges (S1, S2 and S3), but was not detected with calcinated sludges (S1 calcined, S2 calcined and S3 calcined). Some other forms of Fe also occurred in samples (Fe_3O_4 (ICDD 04-006-6551), $CaFeAlO_4$ (ICDD 04-011-5956) and FeSiO (ICDD 01-089-8104)).

In Table 3 are presented results from BET method. As can be seen, specific surface area of samples is significantly reduced as a result of the calcination process. Further, calcination affected the porosity as well. All samples were mostly mesoporous, but calcination decreased microporosity towards mesopores and macropores.

Stability tests

The stability of the sludges was studied in neutral conditions (water) and as a result can be found that only small amount of iron was dissolved to the water and sludges are stable in neutral conditions. Results showed that S2 and S2 calcined were dissolved the highest amount of Fe with 1.31 and 0.95 ppm, respectively, and S3 and S3 calcined had dissolved only a little amount (0.003 and 0.014 ppm, respectively) to the water during the test. Stability was also studied in acidic conditions and results showed that sludges S2 calcined and S3 calcined were most stable while S1, S1 calcined and S3 were leaching iron into the solution. In Table 4 is presented Fe concentration in neutral and acidic conditions for each stability test sample.

These results indicated that sludge is stable in neutral and in acidic conditions. Leaching of iron was lower in S2, S2 calcined and S3 calcined sludges than other sludges that had iron content over 550 ppm. Iron content in S1 calcined sludge was over 10 % higher than in S1 while other calcined sludges, S2 and S3, iron contents were much lower than same non-calcined sludge had. There might be some effect of the ratio of Fe_2O_3, Al_2O_3 and SiO_3 to the results There are studies of CWPO within different ratios where Fe_2O_3 content is less than 20 %, the Al_2O_3 content is slightly higher and SiO_3 was the main element (Barrault et al., 2000; Mûnos et al., 2017). In these studies, the ratio of Fe_2O_3 : Al_2O_3 : SiO_3 have major differences to ratios in this study and are not comparable to each other.

As EC sludge can be modified using different electrodes in water treatment it has many possibilities to make certain type of specially modified adsorbent material easily in EC process. Other novel

approach in this study is finding of the ratio of Fe_2O_3, Al_2O_3 and SiO_3.This ratio may have some influences on adsorption and catalysis, but not any research studies in this area were found. These two findings may create a new production to the low-cost, specially modified adsorbent and catalyst materials from side stream of wastewater purification.

Utilization as adsorbent for humic acid removal

The aim of adsorption test was to find out EC sludge applicability for humic acid removal from water solution and compare three different EC sludges the in same adsorption conditions. The adsorption experiment results with different pH areas are presented in Table 5 as TOC removal. The effect of Fe_2O_3 : Al_2O_3 content in sludges may affect the removal of TC and TOC. Zeng et al. (2013) has studied the ratio of Al-Fe in adsorption and resulted in their study that the higher the aluminum content versus iron content is the higher the adsorption capacity is. Removal % of the TOC (Table 5) were mainly higher with lower pH areas with S1, S2 and S3 sludges. With calcined sludge S1 was no significant changes between pH areas, calcined S2 removal rate increased to pH 7 and decreased in pH 9. The calcined S3 over 90 % of removal all except pH 9 which had value of 84.3 % removal. The humic acid adsorption in different pH areas has been studied by Esfandiar et al. (2022) and Chen et al. (2022) Their experiments showed that alkaline conditions in sorption increases the removal efficiency. Chen et al. (2022) concluded that humic acid increased the removal rate of Cr(VI) in adsorption.

In adsorption the highest TOC removals were with S3 and S3 calcined sludges that had highest Fe_2O_3 contents compared to other non-calcined and calcined sludges. The TOC reduction % is presented in Table 5 The highest removal rates were measured from S3 calcined in pH 3, 5 and 7 over 95 %. The S2 calcined has highest TOC removal value at pH 9.

In Table 6 is presented adsorption capacity [g] of humic acid per 1 g of sample for each tested EC sludge. S3 calcined had the highest adsorption capacity in pH 3 and pH5 over 21 g of humic acid per gram of adsorbent and with higher pH areas (pH 7 and pH 9) S1 calcined had the highest adsorption capacity 21.3 and 20.5, respectively.

In this experiment EC sludge was utilized as adsorbent with good results. Calcinating of sludges make sludge more usable as adsorbent affording to results of this study. As an adsorbent EC sludge has suitable qualities for adsorption utilization of sludge. Important adsorbent qualities are according to Pourhakkak et al. (2021) high efficiency, affordability, reproducibility, and scalability. EC sludge used in this study was formed in mining industry wastewater treatment and sludge formation is a side stream of water purification process which makes it low-cost adsorbent. EC sludge from same source can be modified as used in this study with different electrode materials. Utilization of EC sludge as adsorbent refills all the qualities that are needed for adsorbent. There is a need for further

examination of EC sludge use in adsorption and modification of sludge to use it as more selectivity adsorbent.

Catalytic wet peroxide oxidation experiments

The aim was to study EC sludge's applicability as catalyst in CWPO of BPA. EC sludges S1 calcined, S2 calcined and S3 calcined were used in CWPO tests. All experiments were made with same parameters; 180 minutes of reaction time, BPA concentration 60 mg/L, catalyst load 4g/L and H_2O_2 content 0.15 wt.%. In Figure 3 is presented the results of BPA removal %.

The possible adsorption of BPA was first tested without the addition of oxidizer. According to results only 10% of BPA removal was occurred during 3h experiment. The BPA removal (Figure 3) at the end of experiments with S1 calcined, S2 calcined and S3 calcined were 85 %, 52 % and 34 %, respectively. Juhola et al. (2017) result in their study the highest BPA removal efficiency of 83 %. In their study had similar operational conditions than in this study and used catalyst were iron loaded biomass-based carbon residue. Mena et al. (2017) over 99 % removal rates with their study of Fe catalysts supported on activated carbon with CWPO of BPA. The result of S1 calcined removal rate of BPA is in line with these experiments. The TOC removal in all experiments were between 25 % - 40 %.

The magnetite (Fe_3O_4) and hematite (Fe_2O_3) are usable as iron-based catalyst and sludge from EC system that uses dissolving Fe anodes consist these materials according to the earlier studies of Gomes et al. (2007) and Lineras-Hernandez et al. (2009). Also, aluminum oxides are used as catalyst for their chemical inertness, strength, and hardness. Gomes et al. (2007) and Lineras-Hernandez et al. (2009) defined some aluminum oxide products that are formed in EC like bayerite (α-$Al(OH)_3$). Results in this study shows that calcined EC sludge is utilizable for catalytic use for BPA removal. Further studies for optimal temperature and modifications of EC sludge for catalytic use are needed to get better knowledge and specific modified catalyst to BPA removal. Other catalytic possibilities are also needed to study.

CONCLUSIONS

The aim of the study was to study three EC sludges in two utilization application, as a catalyst and as an adsorbent. The three different EC sludges were used and prepared to test as a raw and a calcined material.

- EC sludge from same source is highly varies from its elements. The elemental analysis is dependent of used electrode materials, current density, and treated water solutions.
- EC sludge as adsorbent is useful and low-cost material. The modification of adsorbent can be made in water purification which makes it interesting to further research area.

- Adsorption test showed good adsorption capacity in different pH areas for synthetic humic acid solution.
- The CWPO of BPA was studied by calcined EC sludges. The S1 calcined sludge showed excellent catalytic activity with the BPA removal of almost 85 % after 3h oxidation reaction.
- As a result, further experiments of EC sludge as catalyst of different applications are needed to find out more utilization possibilities to EC sludge.
- Findings of the modification of the sludge in the EC process with different electrodes, current densities, and treated water solution to different utilization use are novel approach. This needs to be further exanimated.

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DATA AVAILABILITY STATEMENT

All data, models, and code generated or used during the study appear in the submitted article.

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TABLES

Table 1. Calculated amount of sample for each tested material in acidic condition test. The mixing time was 24 h and stirring speed 300 rpm.

Name of the sample	Calculated amount of sample in test (g / L) including 1.77 g / L of Fe_2O_3 (g / L)
S1	3.33
S1 calcined	3.37
S2	3.86
S2 calcined	3.69
S3	2.79
S3 calcined	2.61

Table 2. The X-ray fluorescence (XRF) analysis of the different EC sludges

Sample	S1	S1 calcined	S2	S2 calcined	S3	S3 calcined
Fe_2O_3 (%)	53.1	52.5	45.9	47.9	63.4	67.9
SiO_3 (%)	15.8	17.5	11.7	11.6	2.5	2.0
Al_2O_3 (%)	6.0	6.1	15.3	13.9	14.3	10.0
SO_3 (%)	11.7	9.7	11.6	11.4	8.3	8.5
CaO (%)	4.5	4.6	4.8	4.8	3.3	3.2
WO_3 (%)	1.2	2.3	3.8	3.9	1.3	1.0
ZnO (%)	0.9	0. 9	1.0	0.9	1.8	2.5
MgO (%)	2.1	2.1	2.2	1.9	2.0	1.7
MnO (%)	1.0	1.0	0.9	0.9	1. 6	1.8
P_2O_5 (%)	0.9	1.1	1.1	1.2	1.2	1.2
Total (%)	97.3	97.6	98.3	98.4	99.5	99.7

493 Table 3. BET surface area, total pore volume and pore size distribution by DFT model

Sample	BET [m^2g^{-1}]	PV [cm^3g^{-1}]	Micro [%]	Meso [%]	Macro [%]
S1	146	0.186	12.4	85.5	2.2
S1 calcined	50	0.206	2.4	88.3	9.2
S2	152	0.234	6.4	83.3	10.3
S2 calcined	50	0.205	1.5	89.3	9.3
S3	115	0.213	5.2	85.4	9.4
S3 calcined	47	0.186	1.6	72.6	25.8

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495 Table 4. Fe concentration in neutral and acidic pH conditions after the stability tests

Sample	unit	S1	S1 calcined	S2	S2 calcined	S3	S3 calcined
Fe concen. neutral	ppm	0.449	0.467	1.31	0.95	0.003	0.014
Fe concen. acidic	ppm	556	613	90.2	41.1	594	43.1

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497 Table 5. Total organic carbon (TOC) removal-% in different pH values

Sample	pH 3 %	pH 5 %	pH 7 %	pH9 %
S1	80.8	77.9	68.9	69.0
S1 calcined	87.8	85.8	91.0	86.6
S2	81.7	62.5	62.6	63.7
S2 calcined	76.1	93.3	91.9	93.0
S3	88.4	85.3	76.6	89.0
S3 calcined	95.1	95.9	95.4	92.1

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502 Table 6. Adsorption capacity [g] of humic acid per 1 g of sample sludge.

Sample 1 g	pH 3 [g]	pH 5 [g]	pH 7 [g]	pH 9 [g]
S1	19.1	18.5	16.3	16.4
S1 calcined	20.7	20.3	21.3	20.5
S2	18.2	15.6	15.4	13.9
S2 calcined	17.9	20.2	20.4	20.3
S3	19.7	20.2	18.2	19.9
S3 calcined	21.8	21.3	20.3	19.9

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FIGURE CAPTION LIST

Figure 1. DRIFT spectra of untreated (S1, S2 and S3) and calcined (S1 calcined, S2 calcined and S3 calcined) EC sludges

Figure 2. XRD analysis of untreated (S1, S2 and S3) and calcined (S1 calcined, S2 calcined and S3 calcined) EC sludges. ICDD file 01-077-8621 (SiO_2), ICDD 01-084-2782 (Fe_2O_3), ICDD 04-002-1587 (FeS_2), ICDD 04-015-4421 (Gypsum), ICDD 04-006-6551 (Fe_3O_4), ICDD 04-011-5956 ($CaFeAlO_4$), ICDD 01-089-8104 (FeSiO) and ICDD 04-008-2186 ($CaSO_4$).

Figure 3. The BPA removal % over different EC sludges as a function of the reaction time. S1 cal = calcined S1 EC sludge, S2 = calcined S2 EC sludge and S3 = calcined S3 EC sludge.

Figure 1

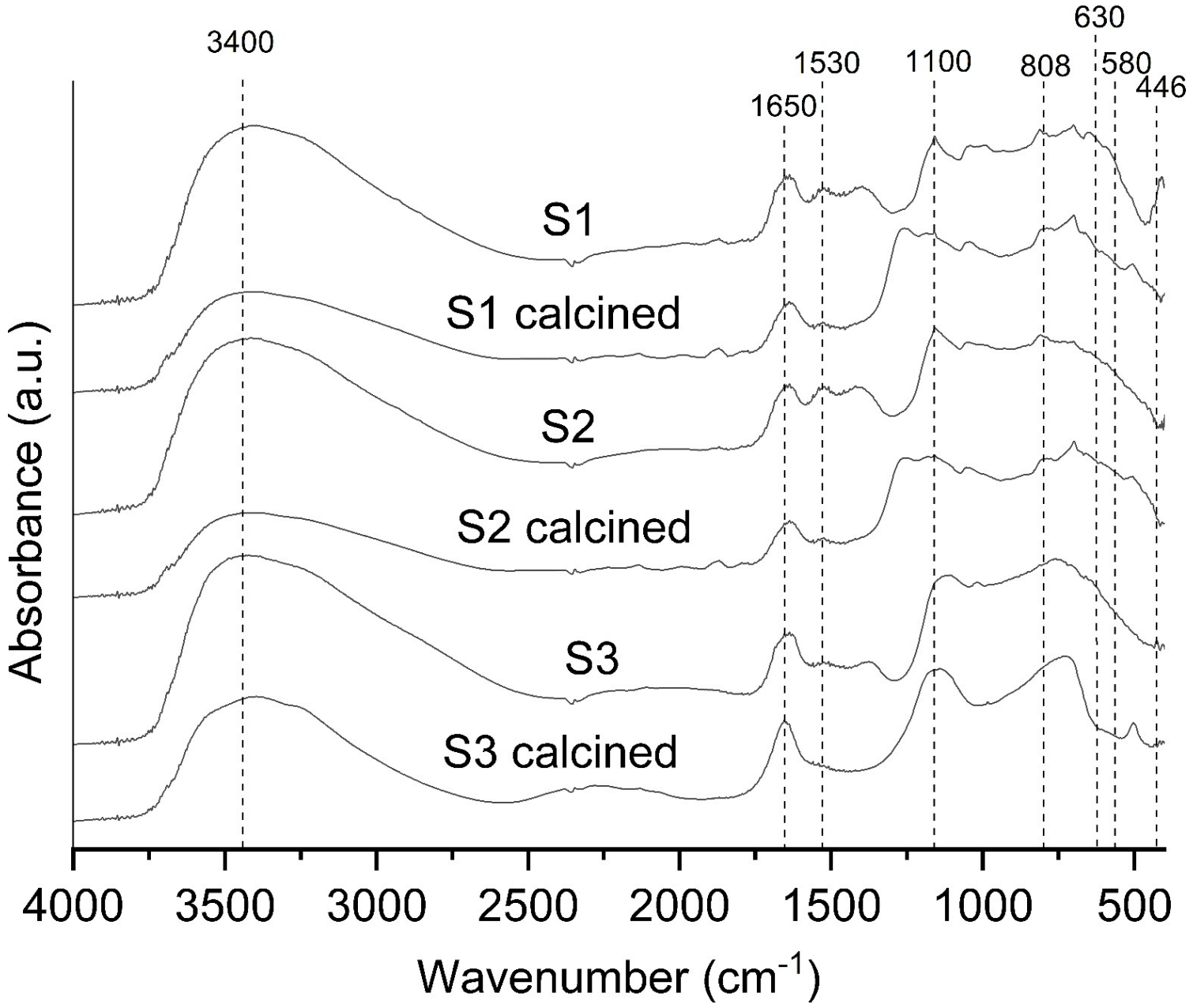

Figure 2

Click here to access/download;Figure;Figure_2.pdf

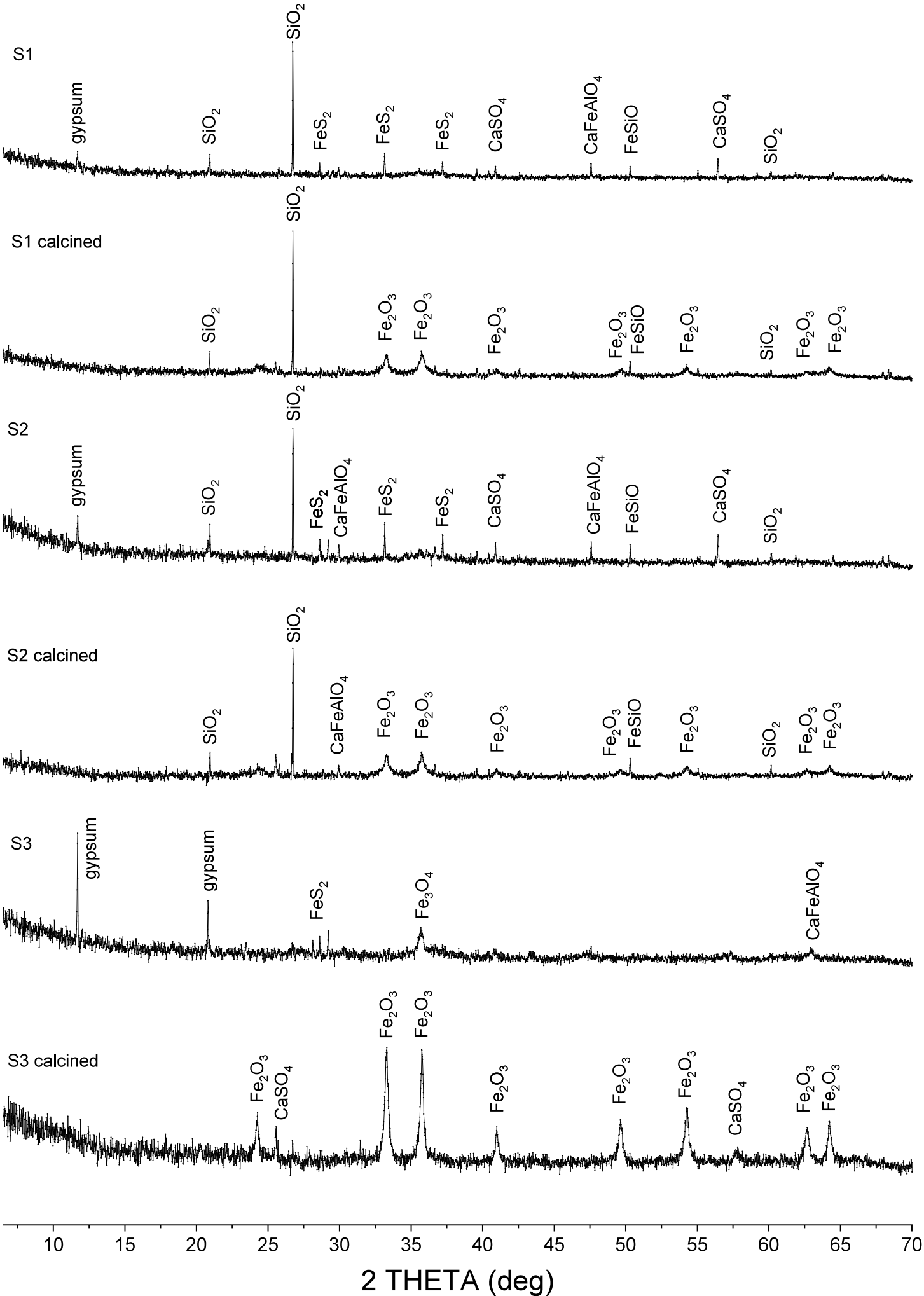

Figure 3