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1 Use of Fe and Al Containing Electrocoagulation Sludge as an Adsorbent and a 2 Catalyst in Water Treatment

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19 **ABSTRACT**

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

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

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

39 **KEYWORDS**

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

41

42 **INTRODUCTION**

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

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

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

80 EC process produces sludge which is not currently efficiently utilized. Depending on electrode
81 material, sludge is usable in different ways as building material, adsorbent, catalyst, pigment, etc.
82 (Rajaniemi et al, 2021a). There are studies of EC sludge in fertilizer use (Rajaniemi et al 2021b, Kruk
83 et al., 2014). These studies have been made with magnesium electrodes and with water that has
84 phosphate and nitrogen content. Iron oxides are used as pigments and EC sludge that has iron
85 oxides can be used as pigment according to Tezcan et al (2017). The EC sludges have some
86 properties that are suitable for non-structural building material use (Adyel et al., 2013; Sharma et al.,
87 2016). Some individual EC sludge studies for suitability for anaerobic digestion during municipal
88 wastewater treatment (Huthan et al. 2006), in ultrasound-mediated Cr(VI) reduction (Kathiravan et
89 al., 2011) and nanocrystalline source material (Li et al., 2013). Commonly used catalysts are iron
90 oxide-based catalysts in various applications. EC sludge can be used as catalyst in different
91 applications like catalyst for peroxydisulphate activation (Ghanbari et al., 2020) or photocatalyst
92 (Shon et al., 2010). The iron oxide-based adsorbents are also widely studied, and EC sludge has
93 been used as adsorbent in some applications like dye (Golder et al., 2006) and fluoride (Yilmaz et al.,
94 2015) removal. It is important to find multiple usage to one sludge to make it more reusable. Iron and
95 aluminum containing sludges were studied in this work, and the potential utilization applications were
96 tested as an adsorbent and catalyst.

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

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

110 **MATERIALS AND METHODS**

111 **Electrocoagulation sludge**

112 Electrocoagulation sludge's properties are strongly depending on electrode material and used
113 current density in the process. Sludge properties are slightly affected from treated water and sludge
114 is more compact than in other treatment methods like chemical precipitation (CP). (Mollah et al.,
115 2001; Sahu et al., 2014). All the three sludges used in this study was collected from continuous EC
116 processes, that is based on patent FI20165317 (Rajaniemi et al. 2016)

117 Sludges from mining industry wastewater treatment pilot plant (MIWTTP) were collected from
118 continuous EC equipment that has maximum treatment capacity of 1.5 m³ per hour. This EC water
119 treatment equipment is in Oulu Mining School pilot process with closed water treatment cycle.
120 Several kinds of mainly metal containing mining waters varied inside of periods of each sludge
121 collection period. The S1 was collected using both Al and Fe sacrificial anodes. The S2 was collected
122 from several different process using mainly Al sacrificial anodes with iron electrodes in the last
123 phase. The S3 had several different process test sludges using mainly Fe sacrificial electrodes. This
124 continuous EC process used five electrode pairs that had treatment area of 0.2 m². The current
125 density in this process was 40 A/m² and used flow has been about 0.9 m³ / h.

126 **Characterization of materials**

127 The sludge from EC equipment was collected from overflow and dried at 105 °C. After drying sludge
128 was crushed and grinded. The sludge analysis in thermogravimetric analysis (Netzsch STA
129 409PC/PG) were defined up to 1000 °C and based on this 550 °C was chosen as calcination
130 temperature, because after that the temperature the change of TG value was almost stable. Some
131 amount of all sludges was calcined at 550 °C for four hours with temperature raise of 1 °C per minute
132 and 2 h stabilization at temperature of 360 °C. All sludges' chemical compositions were analysed
133 with X-ray fluorescence (XRF, PanAnalytical Minipal 4) analysis.

134 The phase composition of EC sludges was analysed by X-ray diffractometer (XRD, PANalytical
135 X'pert Pro X-ray diffractometer) using monochromatic CuK α 1 radiation ($\lambda=1.5406$ Å) at 45 kV and
136 40 mA. The diffractograms were collected in the 2 θ range 6–90° at 0.017° intervals and with scan
137 step time of 100 s. The crystalline phases and structures were analysed by HighScore Plus software
138 using the Powder Diffraction File standards from the International Centre for Diffraction DATA ICDD
139 (PDF-4+ 2020 RDB). Diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) was

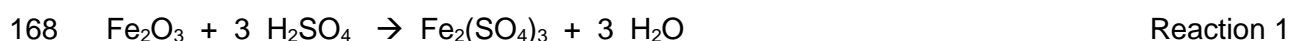
140 used to analyse functional groups on the surface of EC sludges. DRIFT spectra were recorded on a
141 Bruker PMA 50 Vertex 80 V (Bruker, Billerica, MA, United States), equipped with a Harrick Praying
142 Mantis diffuse reflection accessory and a high-temperature reaction chamber, by baseline
143 measurement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

145 Specific surface area (SSA), pore volume (PV) and pore size distribution (PSD) of the samples, were
146 determined at 77.15 K with Micromeritics 3 Flex physisorption instrument (Micromeritics Instruments,
147 Norcross, GA, USA). Exact portions of each sample (100–200 mg) were degassed with Micromeritics
148 smart VacPrep gas adsorption sample preparation device at pressure of 0.67 kPa and at a
149 temperature of 413 K for 3 h to remove impurities. Adsorption isotherms were measured in liquid
150 nitrogen (77.15 K) at constant temperature. Data was processed with 3Flex version 5.02 software.
151 SSAs were calculated from adsorption isotherms based on the Brunauer–Emmett–Teller (BET)
152 method (Brunauer et al., 1938). The model selected to estimate the PSD and PV of the sample
153 materials was density functional theory (DFT) based on a model of independent slit-shaped pores.
154 The pore size distribution was calculated from the individual volumes of micropores, mesopores, and
155 macropores with the DFT model. By using the instrumental setup, micropores down to a diameter of
156 0.35 nm can be measured. A previous study has reported that SSAs are typically measured with a
157 precision of 5% (Hacley and Stefaniak, 2013).

158 Stability tests in neutral and acidic conditions

159 Solubility of the materials were tested in both neutral (water) and acidic (sulfuric acid) conditions. In
160 water leaching test 2.5 g of each sludge was mixed to MilliQ water solution. In acidic leaching
161 experiment solution was made with Milli-Q water and commercial H₂SO₄ (95 wt-%, J.T. Baker). The
162 amount of H₂SO₄ was defined to be 1.77 mL / L at pH 1.5. All the samples were mixed for 24 h with
163 300 rpm and filtered through 0.45 μm filter paper. The iron content of the filtered samples was
164 determined with AAS. All the experiments were duplicated. The pH was measured using Hach
165 HQ30d pH electrode.

166 Under the acidic conditions, the amount of Fe₂O₃ in pH 1.5 was determined to be 1.77 g / L from
167 following reaction 1:



169 Each different sample had different value of Fe₂O₃. In Table 1 is presented the calculated amount of
170 sample for each sample. Fe₂O₃ concentration was defined from elemental analysis of XRF with
171 following equation

$$172 \text{Amount of Fe}_2\text{O}_3 = \frac{\text{wanted amount of Fe}_2\text{O}_3 \text{ 1.77 g/L}}{\text{Fe}_2\text{O}_3 \% \text{ in XRF analysis}} \quad \text{Equation 1}$$

173 where amount of Fe (g / L) is calculated dividing the wanted amount of Fe₂O₃, 1.77 g / L, by wt-% of
174 Fe₂O₃ determined with XRF elemental analysis.

175 The iron content, in all experiments, was analyzed with in ICP-OES analysis (Thermo Electron iCAP
176 6500 Duo, Thermo Fisher Scientific, Waltham, MA, USA). Leaching of the materials was evaluated
177 by using water extraction and acid extraction by mixing materials in the laboratory shaker for 24 h,
178 filtered through 0.45 µm filter paper. After mixing and filtering the Fe concentration was analyzed by
179 AAS. All the experiments were done in duplicate.

180 Use of electrocoagulation sludge as a catalyst in catalytic wet peroxide 181 oxidation

182 All the sample materials were dried, crushed and grinded and finally sieved between 63 – 150 µm
183 particle size. The catalytic wet peroxide oxidation (CWPO) experiments were done to study EC
184 sludge as iron catalyst in the aqueous oxidation of BPA solution. The initial concentration of BPA in
185 the solution was 60 mg / L. The hydrogen peroxide (H₂O₂) concentration in solution was determined
186 to be 0.15 w-%. Three-necked 500 mL round bottom flask was used in the oxidation reaction with
187 the magnetic stirrer. The concentration of catalyst in each different experiment was 4 g/L and added
188 to reactor. 160 mL of BPA solution was added to flask under continuous stirring. The temperature
189 was adjusted at 50 °C and the reaction time was 3 h. Initial sample was collected when solution
190 reached 50 °C. Every 30 min 10 mL sample was taken. and 10 mL of H₂O₂ solution was added. Last
191 addition was made at t = 120 min. All the samples were filtered through 0.45 µm filter paper. The pH
192 and dissolved oxygen content were taken during experiment when sample was collected, and BPA
193 concentration was measured in HPLC from samples. All the experiments were duplicated.

194 Electrocoagulation sludge as an adsorbent in humic acid removal

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

207 RESULTS AND DISCUSSION

208 Characterization of materials

209 In Table 2 is shown the composition of EC sludges determined by XRF. The presented 10 oxides
210 are covering over 97 % of S1 and S1 calcined samples, over 98 % of S2 and S2 calcined and over
211 99 % of S3 and S3 calcined.

212 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 %
213 to 17.48 %. In all samples the combined oxides % of Fe_2O_3 , Al_2O_3 and SiO_3 were between 72 – 80%
214 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
215 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
216 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
217 : Al_2O_3 were in S1 and S1 calcined approximately 58.9 %, S2 and S2 calcined 61.5 % and with S3
218 and S3 calcined 77.8 % of total elemental content.

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

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

242 presence of FeS₂ (Figure 2) and the peaks related to the stretching of S–S and Fe–S can be seen
243 in the DRIFT spectra at wavenumber region 607-622 cm⁻¹ (Siavash et al., 2015) in calcinated
244 samples.

245 XRD patterns of the S1, S1 calcined, S2 and S2 calcined showed high peaks of SiO₂ (ICDD 01-077-
246 8621). In the sludges S1 calcined and S2 calcined Fe₂O₃ (ICDD 01-084-2782) peaks were found
247 while S1 and S2 iron was in form of FeS₂ (ICDD 04-002-1587). S3 calcined sample had clear peaks
248 of Fe₂O₃ and CaSO₄ (ICDD 04-008-2186) while SiO₂ was not clearly in presence. In S1 and S2 had
249 also peaks from CaSO₄. Gypsum (ICDD 04-015-4421) occurred in untreated sludges (S1, S2 and
250 S3), but was not detected with calcinated sludges (S1 calcined, S2 calcined and S3 calcined). Some
251 other forms of Fe also occurred in samples (Fe₃O₄ (ICDD 04-006-6551), CaFeAlO₄ (ICDD 04-011-
252 5956) and FeSiO (ICDD 01-089-8104)).

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

257 Stability tests

258 The stability of the sludges was studied in neutral conditions (water) and as a result can be found
259 that only small amount of iron was dissolved to the water and sludges are stable in neutral conditions.
260 Results showed that S2 and S2 calcined were dissolved the highest amount of Fe with 1.31 and
261 0.95 ppm, respectively, and S3 and S3 calcined had dissolved only a little amount (0.003 and 0.014
262 ppm, respectively) to the water during the test. Stability was also studied in acidic conditions and
263 results showed that sludges S2 calcined and S3 calcined were most stable while S1, S1 calcined
264 and S3 were leaching iron into the solution. In Table 4 is presented Fe concentration in neutral and
265 acidic conditions for each stability test sample.

266 These results indicated that sludge is stable in neutral and in acidic conditions. Leaching of iron was
267 lower in S2, S2 calcined and S3 calcined sludges than other sludges that had iron content over 550
268 ppm. Iron content in S1 calcined sludge was over 10 % higher than in S1 while other calcined
269 sludges, S2 and S3, iron contents were much lower than same non-calcined sludge had. There might
270 be some effect of the ratio of Fe₂O₃, Al₂O₃ and SiO₃ to the results There are studies of CWPO within
271 different ratios where Fe₂O₃ content is less than 20 %, the Al₂O₃ content is slightly higher and SiO₃
272 was the main element (Barrault et al., 2000; Múnos et al., 2017). In these studies, the ratio of Fe₂O₃
273 : Al₂O₃ : SiO₃ have major differences to ratios in this study and are not comparable to each other.

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

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

280 Utilization as adsorbent for humic acid removal

281 The aim of adsorption test was to find out EC sludge applicability for humic acid removal from water
282 solution and compare three different EC sludges the in same adsorption conditions. The adsorption
283 experiment results with different pH areas are presented in Table 5 as TOC removal. The effect of
284 Fe_2O_3 : Al_2O_3 content in sludges may affect the removal of TC and TOC. Zeng et al. (2013) has
285 studied the ratio of Al-Fe in adsorption and resulted in their study that the higher the aluminum
286 content versus iron content is the higher the adsorption capacity is. Removal % of the TOC (Table
287 5) were mainly higher with lower pH areas with S1, S2 and S3 sludges. With calcined sludge S1 was
288 no significant changes between pH areas, calcined S2 removal rate increased to pH 7 and
289 decreased in pH 9. The calcined S3 over 90 % of removal all except pH 9 which had value of 84.3
290 % removal. The humic acid adsorption in different pH areas has been studied by Esfandiar et al.
291 (2022) and Chen et al. (2022) Their experiments showed that alkaline conditions in sorption
292 increases the removal efficiency. Chen et al. (2022) concluded that humic acid increased the removal
293 rate of Cr(VI) in adsorption.

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

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

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

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

312 Catalytic wet peroxide oxidation experiments

313 The aim was to study EC sludge's applicability as catalyst in CWPO of BPA. EC sludges S1 calcined,
314 S2 calcined and S3 calcined were used in CWPO tests. All experiments were made with same
315 parameters; 180 minutes of reaction time, BPA concentration 60 mg/L, catalyst load 4g/L and H₂O₂
316 content 0.15 wt.%. In Figure 3 is presented the results of BPA removal %.

317 The possible adsorption of BPA was first tested without the addition of oxidizer. According to results
318 only 10% of BPA removal was occurred during 3h experiment. The BPA removal (Figure 3) at the
319 end of experiments with S1 calcined, S2 calcined and S3 calcined were 85 %, 52 % and 34 %,
320 respectively. Juhola et al. (2017) result in their study the highest BPA removal efficiency of 83 %. In
321 their study had similar operational conditions than in this study and used catalyst were iron loaded
322 biomass-based carbon residue. Mena et al. (2017) over 99 % removal rates with their study of Fe
323 catalysts supported on activated carbon with CWPO of BPA. The result of S1 calcined removal rate
324 of BPA is in line with these experiments. The TOC removal in all experiments were between 25 % -
325 40 %.

326 The magnetite (Fe₃O₄) and hematite (Fe₂O₃) are usable as iron-based catalyst and sludge from EC
327 system that uses dissolving Fe anodes consist these materials according to the earlier studies of
328 Gomes et al. (2007) and Lineras-Hernandez et al. (2009). Also, aluminum oxides are used as
329 catalyst for their chemical inertness, strength, and hardness. Gomes et al. (2007) and Lineras-
330 Hernandez et al. (2009) defined some aluminum oxide products that are formed in EC like bayerite
331 (α -Al(OH)₃). Results in this study shows that calcined EC sludge is utilizable for catalytic use for BPA
332 removal. Further studies for optimal temperature and modifications of EC sludge for catalytic use are
333 needed to get better knowledge and specific modified catalyst to BPA removal. Other catalytic
334 possibilities are also needed to study.

335 CONCLUSIONS

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

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

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

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358 **DATA AVAILABILITY STATEMENT**

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

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483

484 **TABLES**

485 Table 1. Calculated amount of sample for each tested material in acidic condition test. The mixing
 486 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 ₂ O ₃ (g / L) |
|--------------------|------------------------------------------------------------------------------------------------------------|
| S1 | 3.33 |
| S1 calcined | 3.37 |
| S2 | 3.86 |
| S2 calcined | 3.69 |
| S3 | 2.79 |
| S3 calcined | 2.61 |

487

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

| Sample | S1 | S1 calcined | S2 | S2 calcined | S3 | S3 calcined |
|------------------------------------|------|-------------|------|-------------|------|-------------|
| Fe ₂ O 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 ₂ O 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 ₂ O 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 |

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

| Sample | BET [m ² g ⁻¹] | PV [cm ³ g ⁻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 |

494

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 |

496

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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505 **FIGURE CAPTION LIST**

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

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

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

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