

1 **Removal of metals from wastewaters by mineral and biomass-based sorbents applied in**
2 **continuous-flow continuous stirred tank reactors followed by sedimentation**

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10 **Abstract:** Numerous studies have examined the performance of mineral and biomass-based sorbents
11 for metal removal under laboratory conditions, but few pilot-scale tests have been performed on
12 possible water purification systems in which these sorbents can be used. This study addressed this
13 issue by evaluating the suitability of selected sorbents for use in continuous-flow continuous stirred
14 tank reactors (CSTR) followed by sedimentation in laboratory and in situ pilot-scale experiments. Acid
15 (HCl)-modified peat (M-Peat), a commercially available mineral sorbent containing mainly
16 magnesium (Mg) carbonates, Mg oxides and Mg silicates (Mineral-P) and a calcium-rich ground
17 granular blast furnace slag (by-product of stainless steel production (Slag) were tested for treatment of
18 metallurgical industry wastewater (laboratory, pilot). Overall, higher metal removal was achieved from
19 samples with higher initial metal concentrations. M-Peat achieved good removal of Zn (50-70%) and
20 Ni (30-50%) in laboratory and pilot experiments. However, the poor settling characteristics of M-Peat
21 can restrict its application in systems where sedimentation is the solid-liquid separation process
22 applied. Mineral-P showed good performance in removing 65-85% of Zn present in the water and it
23 performed similarly in laboratory and pilot tests. However, low concentrations of As and Ni leached
24 from Mineral-P in all tests. Slag achieved good performance in treatment of the industrial wastewater,

25 removing 65-80% of Zn and 60-80% of Pb during pilot tests. However, low concentrations of Cr and
26 Cu were leached from Slag in a few tests. As a by-product of the same (metallurgical) industry, ground
27 granular blast furnace slag is an excellent candidate for reducing Zn concentrations from industrial
28 wastewater flows.

29 **Keywords:** low-cost sorbents, byproduct, pilot tests, biosorbents, industrial wastewater

30 1. Introduction

31 Release of metals into the environment from a number of point sources (industrial etc.) and diffuse
32 sources (urban runoff, mining drainage etc.) can impair surface water quality and can have detrimental
33 effects on receiving aquatic ecosystems and on human health (Schaller et al., 2011). Some metals (and
34 metalloids), such as zinc (Zn), nickel (Ni), cadmium, lead (Pb), chromium (Cr), arsenic (As) etc., are
35 a particular concern because of their toxicity and persistence (Roeva et al., 1996; Schaller et al., 2011).
36 A specific commonality of metal-containing water flows is temporal variation in the type and
37 concentration of metals present and in the discharge volume. Therefore, water treatment processes
38 aimed at reducing metal loads into the environment must cope with water amount and quality
39 variations. Several technologies are available for the removal of metals, such as chemical precipitation,
40 ion exchange, adsorption, membrane filtration and coagulation-flocculation (Barakat, 2011;
41 Hargreaves et al., 2018; Kasiuliene et al., 2018). Chemical precipitation is suitable for higher metal
42 concentrations whereas ion exchange and adsorption using activated carbon would perform well for
43 industrial water having rather low metal concentrations and fluctuating water quality. However, the
44 use of ion exchange resins and activated carbon is limited by the cost of commercial materials.
45 Membrane filtration for metal removal has become widespread in recent years but, it can still be
46 considered an expensive method to treat industrial effluents unless water is recycled back to the process
47 (Barakat, 2011). Coagulation-flocculation process is capable of effectively removing trace metals from
48 wastewaters (Hargreaves et al., 2018) however, it requires monitoring for possible coagulant residues

49 and adjustment of coagulant dosing when water quality varies greatly. Adsorption represents an
50 attractive alternative especially if the adsorbent is inexpensive. It has a number of advantages
51 compared with above mentioned methods, e.g. low implementation costs, it does not produce harmful
52 wastes, it is flexible and normally easy to operate and it is not sensitive to toxic pollutants
53 (Ahmaruzzaman, 2011; Fu and Wang, 2011; Kasiuliene et al., 2018).

54 There has been a clear effort from the research community to develop and test low-cost sorbents based
55 on e.g. biomass materials, waste products from a number of industries, activities and processes, etc.
56 (e.g. Ahmaruzzaman, 2011; Nguyen et al., 2013; Grace et al., 2016). Several studies have examined
57 the performance of low-cost sorbents for metal removal under laboratory conditions (Hlihor and
58 Gavrilescu, 2009; Fu and Wang 2011; Iakovleva, 2013; De Gisi et al., 2016). However, studies on the
59 simultaneous adsorption of mixed heavy metals from real wastewater samples and on possible
60 wastewater purification systems in which these sorbents can be used are more difficult to find (Eger et
61 al., 2015; Kumar et al., 2016). Evaluation of sorbent performance based on investigations using
62 laboratory-scale batch experiments and synthetic metal solutions can result in over- or underestimation
63 of sorbent sorption capacity. This can lead to erroneous assessment of the sorbent's suitability for
64 application in real wastewater treatment systems. For example, the adsorption capacity of target metals
65 is often reported to be generally higher for batch than column experiments, and overall lower for
66 mixed-metal (synthetic or real wastewater) solutions than for single-metal solutions (Reddad et al.,
67 2003; Huber et al., 2016; Kumar et al., 2016; Nguyen et al., 2013~~8~~; Gogoi et al., 2018b). It is also often
68 reported that lower pollutant removal efficiency is achieved in pilot-scale tests than in preliminary
69 laboratory batch-based tests (Zouboulis et al., 2002; Reddy et al., 2014; Postila et al., 2019).

70 Therefore, while it is commonly accepted that there is substantial potential for use of low-cost sorbents
71 in water and wastewater treatment processes (Fu and Wang, 2011; Nguyen et al., 2013; Grace et al.,
72 2016), for this perceived potential to be met, larger numbers of studies applying proof-of-concept and
73 pilot-scale experiments where real wastewater samples are purified are needed (Grace et al., 2016;

74 Malik et al., 2017). In this study, the widely available low-cost sorbents sawdust, peat (biomass-based)
75 and ground granular blast furnace slag (GGBS, by-product of stainless steel production) were tested
76 against a commercially available mineral sorbent. The novelty of this work lies in the experimental
77 techniques and purification system used. These included proof-of-concept laboratory-scale and in situ
78 pilot-scale tests of continuous-flow continuous stirred tank reactors (CSTR), followed by
79 sedimentation (for sorbent water separation). To our knowledge, use of low-cost sorbents in
80 continuous-flow CSTRs coupled with a sedimentation step has not been studied previously. In
81 addition, the effectiveness of GGBS in removal of metals from mixed-metal real wastewater samples
82 has not been fully explored (Grace et al., 2016; Nguyen et al., 2018).

83 Regarding the sorption properties of sorbents tested. The main constituents of peat and sawdust are
84 lignin, cellulose and different humic substances. These constituents contain functional groups such as
85 carboxyl and hydroxyl, which are associated with good sorption capacity (Bulgariu et al., 2011;
86 González and Pokrovsky, 2014; Bartczak et al., 2017). Although natural peat has been found to possess
87 good sorption capacity for metal and metalloids (Brown et al., 2000), a variety of treatments (physical,
88 chemical etc.) have also been investigated with the aim of further increasing their ability to sorb these
89 pollutants. For example, chemical treatment has been applied to enhance the physical-chemical
90 properties of peat and to improve its sorption capacity by ionisation of functional groups (Batista et
91 al., 2009; Leiviskä et al., 2018). GGBS is a waste product of the steel production industry composed
92 mostly of calcium and silicon. Globally, over a billion tonnes of steel are manufactured per annum,
93 leading to the availability of large amounts of GGBS (Juckes, 2011). The high activity of slags
94 regarding adsorption of nonferrous and metal ions can be attributed to the electrochemical
95 heterogeneity of their surface and the high content of easily hydrolysed calcium silicates (Dimitrova,
96 1996, 2002).

97 This study aimed to address the clear gap that exists between evaluation and development of low-cost
98 sorption materials and their practical application in wastewater treatment processes. To achieve this

99 goal, the selected sorbents were tested for removal of metals from real industrial (metallurgical) water
100 samples in laboratory and in situ pilot-scale (macrocosm) continuous-flow CSTR systems.

101 **2. Materials and methods**

102 The research was conducted in two phases. 1) Laboratory (proof-of-concept) evaluation of sorbents
103 applied in a CSTR followed by sedimentation for metal removal from industrial wastewater. The
104 materials evaluated were a commercially available sorbent (PalPower M10, Aqua Minerals Finland
105 Oy, hereafter referred to as Mineral-P), HCl-treated peat (Stora Enso Veitsiluoto Mill, hereafter
106 referred to as M-Peat). 2) Evaluation of sorbents in an in-situ pilot-scale continuous-flow CSTR system
107 coupled with a sedimentation unit for the treatment of industrial wastewater. The sorbents tested were
108 M-Peat, Mineral-P and ground granular blast furnace slag a fine powder, non-hazardous by-product
109 material (Outokumpu Chrome Oy, hereafter referred to as Slag). This study was conducted as part of
110 the HuJa (ERDF) project “Enhancing the treatment of metal-containing storm-waters and wastewaters
111 using natural materials”. Material selection was based on preliminary laboratory studies (Gogoi et al.,
112 2018b) and suggestions from project collaborators.

113 **2.1 Characteristics of the water samples tested**

114 *Phase I – Laboratory tests*

115 An industrial wastewater sample (metallurgical, 100 L) was collected from the inlet of a small retention
116 basin owned by the company Outokumpu Chrome Oy in Tornio, Finland. The basin holds water from
117 the gas-scrubbing unit of the smelting phase of the ferrochrome production process. The collected
118 sample was stored at 5-10 °C for the duration of the tests (4 weeks).

119 Analysis of metal concentrations in raw water samples was carried out by a certified laboratory (SFS-
120 EN ISO 17294-2:2005). The raw samples were divided in two sub-samples, one of which was filtered
121 (syringe filtration, GF 0.45 µm, dissolved concentrations) and the other left unfiltered (total

122 concentration). Analysis was conducted for elemental As, Cd, Cr, copper (Cu), Pb, Ni and Zn. In
123 addition, raw water samples were analysed at our in-house laboratory for: 1) turbidity (EN 27027:1994;
124 Hach Ratio/XR Turbidity meter), 2) pH (SFS-EN 13037:1994; WTW Universal Meter Multiline P4
125 Sensor: WTW Electrode Sentix 81) and 3) dissolved organic carbon (DOC) (Sievers 900 Portable TOC
126 Analyser). The samples were filtered (GF 0.45 μm , syringe filtration) prior to DOC analyses and the
127 manufacturer's instructions were followed.

128 *Phase 2 – In situ pilot tests*

129 Pilot experiments were conducted at the Outokumpu Chrome Oy facilities in Tornio, Finland. Inflow
130 water for the pilot-scale tests was pumped from the same sedimentation basin from which samples
131 were collected for the laboratory tests. Inflow water samples were collected periodically and sent to a
132 certified laboratory for metal composition analysis (SFS-EN ISO 17294-2:2005 and SFS-EN ISO
133 11885:2009) (As, aluminium (Al), Cd, cobalt (Co), Cr, Cu, iron (Fe), Pb, Ni, Zn, etc.) (full list of
134 elements analysed Table S1 in Supplementary Material). The first and last inflow samples collected
135 during tests with each sorbent were divided into two sub-samples, one of which was filtered (syringe
136 filtration, GF 0.45 μm , dissolved concentrations) and one left unfiltered (total concentration), before
137 being sent to the outsourced laboratory. The unfiltered sub-samples were also analysed for suspended
138 solids (SS) (GF 1.2 μm filtration) at our in-house laboratory (SFS-EN 872:2005). Electrical
139 conductivity (EC) (HOBO-logger) and pH (WTW Multi 350i) were continuously monitored.

140 **2.2 Laboratory test procedures**

141 Jar-test methodology was used to simulate the mixing and sedimentation stages of a CSTR followed
142 by sedimentation. The equipment used (Fig. S1a) was a six (1-L) jar programmable paddle stirrer
143 Flocculator 2000 (Kemira Kemwater). The required dosage of sorbents for effective purification of
144 industrial wastewater samples and the contact time (mixing time) needed were identified during a
145 preliminary study (Gogoi et al., 2018b). The materials evaluated and dosage applied for purification

146 of the industrial wastewater sample were M-Peat 0.5 g/L and Mineral-P 0.2 g/L. The required dose of
147 individual sorbents was added to water (1 L) and mixing was applied (15 min, 40 rpm). Once the
148 mixing stopped, the mixer was removed, the sorbent particles were allowed to sediment for 30 min
149 and 250-300 mL of supernatant water were collected (2 cm below the surface) using a pipette (2
150 replicates). Part of the supernatant water sample was analysed at our in-house laboratory for turbidity,
151 pH and DOC (following procedures reported in section 2.1). The remaining supernatant water was
152 divided into two sub-samples, one of which (sub-sample 1) was filtered (GF 0.45 μm , dissolved
153 concentrations, two replicates) and one of which (sub-sample 2) was left unfiltered (total
154 concentrations, one replicate). These were sent to the out-sourced laboratory for metal analyses.

155 To assess the possibility of sorbent recovery and re-use, the sorbents applied in all laboratory
156 experiments were retrieved. After the supernatant water was extracted, the contents (water and
157 sorbents) of individual jars were transferred to centrifuge bottles and centrifuged for 5 min at 4500
158 rpm. The remaining supernatant water was removed and discarded and the sorbents were placed in
159 wide, shallow aluminium dishes, which were loosely covered to allow drying at room temperature (20
160 ± 3 °C). Recovered sorbents from replicates of the same treatment were mixed together and re-applied
161 in a new test following the jar-test procedure described previously (1 replicate). Recovered sorbents
162 are hereafter identified by the addition of a capital “R” after the respective sorbent’s name, e.g. M-Peat
163 R etc.

164 The settling characteristics of the materials tested were evaluated following the methodology outlined
165 in Bratby (2006). Jar-test experiments were performed following the procedure described previously
166 apart from the fact that 30-mL samples were collected at constant jar depth (8 cm from the bottom) at
167 pre-determined intervals (1, 2, 3, 4, 6, 8, 11, 14, 17, 25 min.) during the sedimentation stage of the
168 treatment (2 replicates). Turbidity measurements were performed on the collected samples and used
169 as an indicator of the concentration of particles in suspension.

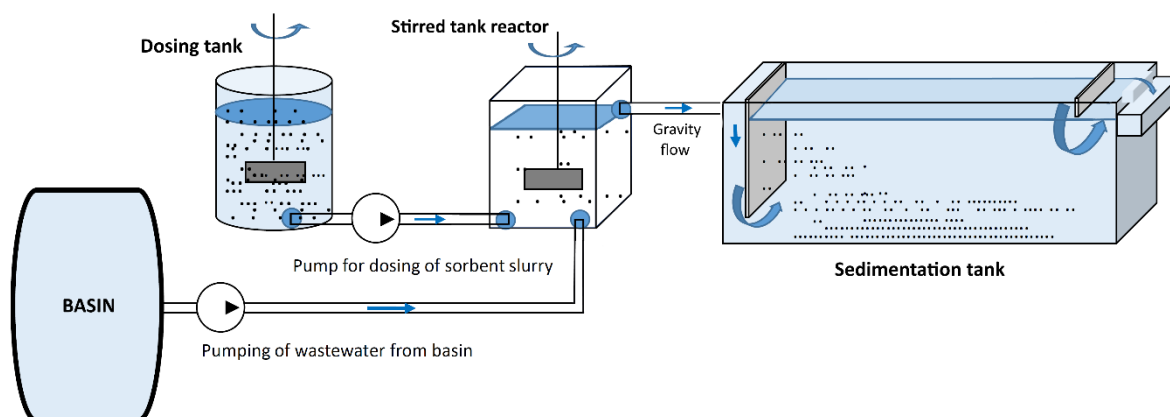
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171 2.3 Pilot test

172 A pilot-scale continuous-flow CSTR system coupled with a sedimentation unit was designed, built and
173 pre-tested at the University of Oulu. The pilot system was then transferred to the Outokumpu Chrome
174 Oy facilities in Tornio. The test period lasted for about four weeks. Evaluated sorbents were Mineral-
175 P, Slag and M-Peat. Slag was not evaluated during the laboratory phase of experiments. Suitable
176 dosage (0.15 g/L) and shortest retention time (15 min) for effective removal of metals by Slag were
177 identified in batch test experiments.

178 2.3.1 Pilot design

179 The pilot system consisted of three separate units, a dosing tank, a stirred tank reactor and a
180 sedimentation tank (Fig. 1). A slurry of the sorbents was prepared in the dosing tank and the suspension
181 was dosed (pumped) to the stirred tank at pre-determined volumetric rates to provide the required
182 sorbent dosage in mg/L of wastewater being treated (Table 1). Wastewater was pumped from the
183 retention basin to the stirred tank reactor. The suspension containing the wastewater and the dosed
184 sorbents was transferred by gravity from the stirred tank reactor to the sedimentation tank (Fig. 1).
185 Dimensioning of the pilot (Table 1) was done using parameters identified during batch experiments
186 (retention time, dosage of sorbents etc.) and general guidelines for the dimensioning of stirred tank
187 reactor and sedimentation units (geometry, geometric ratios, mixers dimensions, etc.) (Reynolds and
188 Richards, 1996).



189

190 Figure 1 – Schematic drawing of the pilot continuous-flow continuous stirred tank reactor (CSTR)
 191 system and sedimentation unit.

192 Table 1. Dimensioning and operational parameters of the continuous stirred tank reactor (CSTR)
 193 system and sedimentation unit (D = diameter of unit, H = height, W = width, d = stirrer diameter, w =
 194 stirrer width, V_{total} = total volume of unit and V_{used} = volume of unit used according to water level
 195 maintained)

Unit	Geometry	Dimensions	Other features	Retention time (Tr)
Dosing tank	Circular	D = 29.5 cm H = 39.5 cm V_{total} = 27 L V_{used} = 22.5 L	Paddle stirrer d = D/3 = 10 cm w = d/4 = 2.5 cm Baffles (4) L = D/10 = 3 cm	According to slurry concentration and dose of sorbent
Stirred tank	Rectangular	W = 25 cm L = 25 cm H = 40 cm V_{total} = 25 L V_{used} = 16.5 L	Paddle stirrer d = W/3 = 8 cm w = d/4 = 2 cm	Tr = 15 min
Sedimentation tank	Rectangular	W = 20 cm L = 120 cm H = 40 cm V_{total} = 95 L V_{used} = 70 L	Flow barrier at 5 cm from inlet and 10 cm from bottom. Surface barrier at 15 cm from outlet and 3 cm of submergence	Tr = 60 min
Sorbent	Target dosage (g/L)	Q wastewater (L/min)	Test period (h) and comments	
Mineral-P	0.15	1.1	120 (3 interruptions)	
M-Peat	0.50	1.1	21 (short due to available mass of product)	
Slag	0.15	1.1	165 (1 interruption)	

196 2.3.2 Operation and monitoring

197 The pilot system was installed on a wooden platform beside the sedimentation basin from which the
 198 wastewater was pumped. At the start of tests, the sedimentation tank and stirred tank were filled with
 199 wastewater. A slurry of the sorbents was prepared by mixing potable water and pre-weighed amounts
 200 of sorbents. Volumetric rate of the dosing pump was set according to the concentration of the slurry
 201 and the required sorbent dosage to be added (Table 1). Electrical conductivity (HOBO-loggers) and
 202 pH (WTW Multi 350i) sensors were placed at the inflow and outflow pipes for continuous monitoring

203 and recording of data (15-min intervals). The system was initiated by starting the dosing of sorbent
204 into the stirred tank. Total wastewater retention time in the systems was around 75 min. Inflow samples
205 were thus collected 75 min before outflow samples so that water retention time in the system was taken
206 into consideration. Inflow and outflow water samples were collected 2 h after start-up and daily for the
207 duration of the test. In cases where interruption of operation occurred (e.g. due to power failure etc.),
208 the start-up procedure was repeated. Outflow water samples were collected using the sampling and
209 analysis procedures described in section 2.1.

210 **2.4 Characterisation of sorbents tested**

211 Natural peat destined for energy production was used for the modification process. Its particle size
212 range was 90-250 μm and the measured ash content was $\sim 10\%$ (Gogoi et al., 2018a). The peat was
213 chemically treated using HCl at 25 $^{\circ}\text{C}$ (for detailed procedure, see Gogoi et al., 2018b), a treatment
214 aimed at decreasing the natural hydrophobicity of the peat and improving its poor settling properties
215 (Leiviskä et al., 2018). Furthermore, the acid treatment was intended to result in desorption of metal
216 ions normally present in natural peat, thus potentially increasing its metal uptake capacity. A full
217 characterisation of the fresh biosorbent material M-Peat (before and after acid treatment) can be found
218 in Gogoi et al. (2018b). Characterisation of the sorbents used in the pilot phase of the study was
219 performed using fresh (Mineral-P and Slag) and recovered/used samples (Mineral-P R, Slag R, M-Peat
220 R) of the materials. Fresh samples of each sorbent were set aside beforehand, while used materials
221 were recovered during the pilot experiments for analysis. For that purpose, sediments (sorbents) that
222 accumulated at the bottom of the sedimentation tank were collected at the end of the test period with
223 each material. Prior to collection of the sorbent samples, the sedimentation tank was drained and the
224 sediment was mixed and homogenised.

225 Elemental composition of fresh and used (pilot) mineral-based materials was analysed as follow;
226 Materials were first crushed to <2 mm grain size ($>80\%$) with a Rocklabs Boyd Crusher. Crushed

227 samples were pulverised to <75 um with an Essa LM2 mill (>95%). The samples were then mixed
228 with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The molten
229 melt was immediately poured into a solution of 5% nitric acid containing an internal standard and
230 mixed continuously until completely dissolved (~30 minutes). The samples were analysed for major
231 oxides and trace elements with inductively coupled plasma optical emission spectrometry (ICP-OES;
232 Varian Vista 735 ICP) and inductively coupled plasma mass spectrometry (ICP-MS; Perkin Elmer
233 Sciex ELAN 9000). 2) X-ray diffraction (XRD) analysis of fresh materials was performed using a
234 Panalytical X'Pert Pro diffractometer equipped with Cu X-ray source and an X'Celerator detector. The
235 XRD patterns were recorded in the 2θ range of 5-70° with a step size of 0.017°. The recovered used
236 sample of M-Peat was submitted to Fourier transform infrared spectroscopy (FTIR) analysis following
237 the procedures outlined in Gogoi et al (2018b).

238 **3. Results**

239 **3.1 Water quality**

240 Water quality characteristics of the industrial wastewater samples used during the laboratory and pilot
241 phases of the study differed significantly in terms of metal concentration, pH, electrical conductivity,
242 etc. (Table 2). Because of the different characteristics of the wastewater samples, fluctuations in
243 purification efficiency and sorbent performance were to be expected. Fluctuations were actually
244 observed during the pilot experiments, as the quality of the inflow water changed significantly during
245 the test period, resulting in high standard deviation for the reported mean values of measured inflow
246 concentrations (Table 2).

247

248 Table 2. Characteristics of the industrial wastewater water samples treated in laboratory experiments
 249 and pilot tests (mean \pm standard deviation (std.), n = number of analysis). Total concentrations (conc.)
 250 and dissolved (dis.) concentrations presented when applicable.

251

Parameter	Industrial wastewater laboratory (total conc.)	Industrial wastewater laboratory (dis. conc.)	Industrial wastewater pilot test (total conc.)	Industrial wastewater pilot test (dis. conc.)
			Mean \pm Std. n = 18	Mean \pm Std. n = 6
As ($\mu\text{g/L}$)	3.7	3.6	2.7 \pm 0.7	1.8 \pm 0.3
Cd ($\mu\text{g/L}$)	0.051	0.027	0.198 \pm 0.170	0.025 \pm 0.000
Cr ($\mu\text{g/L}$)	30.8	17.4	235 \pm 330.6	6.3 \pm 1.8
Cu ($\mu\text{g/L}$)	5.8	1.5	17.8 \pm 25.3	9.1 \pm 15.5
Pb ($\mu\text{g/L}$)	5.9	2.9	25.5 \pm 16.9	4.1 \pm 3.1
Ni ($\mu\text{g/L}$)	42.4	41.9	35.9 \pm 5.2	33.9 \pm 3.8
Zn ($\mu\text{g/L}$)	578	576	3629 \pm 1838	2959 \pm 1915
DOC (mg/L)		0.0		
EC (mS/cm)	2.36		*0.14-1.3	
pH	7.3		*6.5-9.1	
SS (mg/L)			**11.0 \pm 9.4	
Turbidity (NTU)	10.2			

252 *Continuous measurement (15 min intervals). Minimum and maximum recorded values presented. **Number of samples
 253 n = 6.

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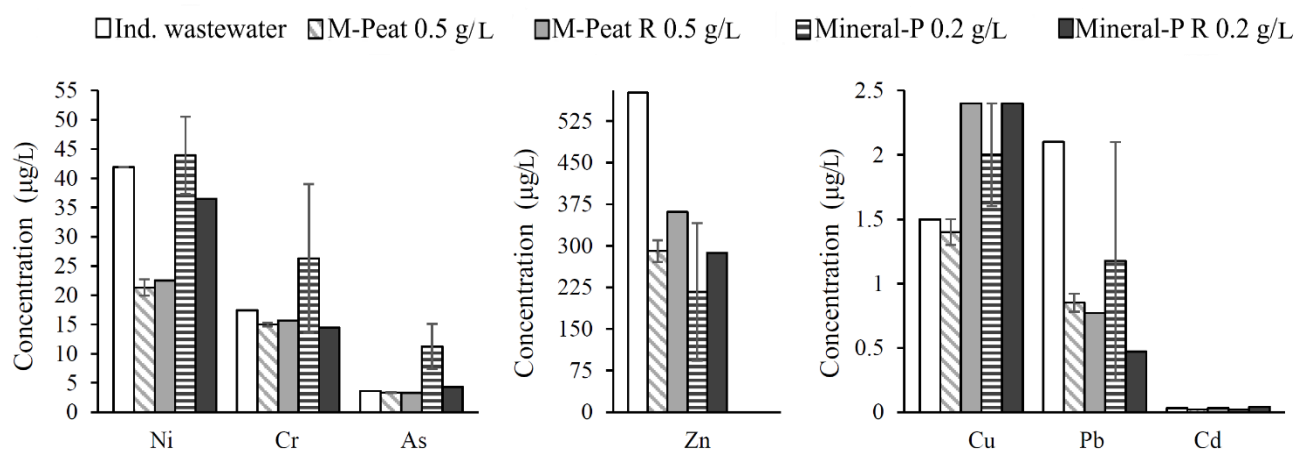
255 3.2 Laboratory tests

256 *Purification efficiency*

257 Under laboratory conditions, the sorbents were tested using the jar-test methodology as a proof of
 258 concept for a CSTR system coupled with sedimentation. The target pollutant in purification of the
 259 industrial wastewater was Zn (other elements were also monitored and reported), as the ferrochrome
 260 production company is required to meet the Zn discharge limits stipulated in their environmental
 261 permit (limit for combined load of all process units of 4kg/day). Regarding removal of the dissolved
 262 fraction of metals, good removal of Ni, Zn and Pb was achieved (Fig. 1a). Overall, M-Peat (0.5 g/L)
 263 achieved higher removal of Pb and Ni, while Mineral-P (0.2 g/L) removed more Zn. Some leaching of
 264 As and Cu from the Mineral-P material was observed. The dosing of sorbents affected water quality
 265 during the experiments, which may also have affected metal concentrations in treated samples. For

266 example, the added dose of Mineral-P increased the pH of the industrial wastewater to values around
 267 8.4 (initial pH 7.3), while addition of M-Peat did not affect the water pH.

268 Regarding the performance of recovered materials, M-Peat R achieved similar removal of Ni, Cr, As
 269 and Pb as fresh M-Peat. At the same time, a small decrease in the removal of Zn (~15%) and leaching
 270 of previously adsorbed Cu occurred (Fig. 2). Addition of Mineral-P R led to similar removal of Ni, Cr,
 271 Cu, Zn and Pb (within the variation of removal rates observed in replicates conducted with the fresh
 272 product), while lower leaching of As occurred. Addition of Mineral-P R increased the pH of the
 273 industrial wastewater from ~7.2 to around 8.0. Thus, the pH increase was not as pronounced as with
 274 use of fresh sorbent (pH ~8.3).



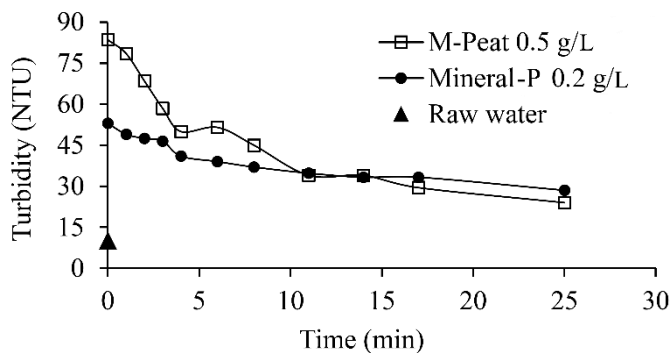
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 276 Figure 2 – Average concentration of dissolved metals in the raw and treated samples of industrial
 277 wastewater and the dose of sorbents used (error bars indicate maximum and minimum values of
 278 experiment replicates).

279 Supernatant water collected after treatment (one replicate) was sent for analysis without filtration
 280 together with raw water samples, in order for total concentrations of the metals (and metalloids) present
 281 to be evaluated. The majority of As, Ni and Zn contained in the industrial wastewater was in solution,
 282 while the other elements analysed were present in dissolved and particulate species in different ratios.
 283 In the treated samples, total concentrations were significantly higher than dissolved concentrations in
 284 samples treated by all sorbents, but especially by Mineral-P (Table S2). This is most likely due to the

285 presence of sorbent particles in the supernatant water, which did not sediment in the provided settling
 286 time and remained in suspension. Moreover, formation of metal precipitate complexes, which also
 287 remain in suspension, cannot be disregarded (Balintova et al., 2012, Haas et al., 2019).

288 *Settling characteristics of sorbent particles*

289 When evaluating the suitability of sorbents for application in CSTR systems coupled with
 290 sedimentation, an important factor to be investigated is the settling characteristics of sorbent particles
 291 in water. Regarding the data presented in Fig. 3, turbidity at time 0 min reflects the turbidity of samples
 292 at the exact moment mixing was stopped, when all particles remained in suspension. Addition of M-
 293 Peat and Mineral-P increased the initial turbidity of the wastewater samples significantly (Fig. 3).
 294 Turbidity decreased with the provided settling time, but it did not reach values close to the turbidity of
 295 untreated water (Fig. 3).



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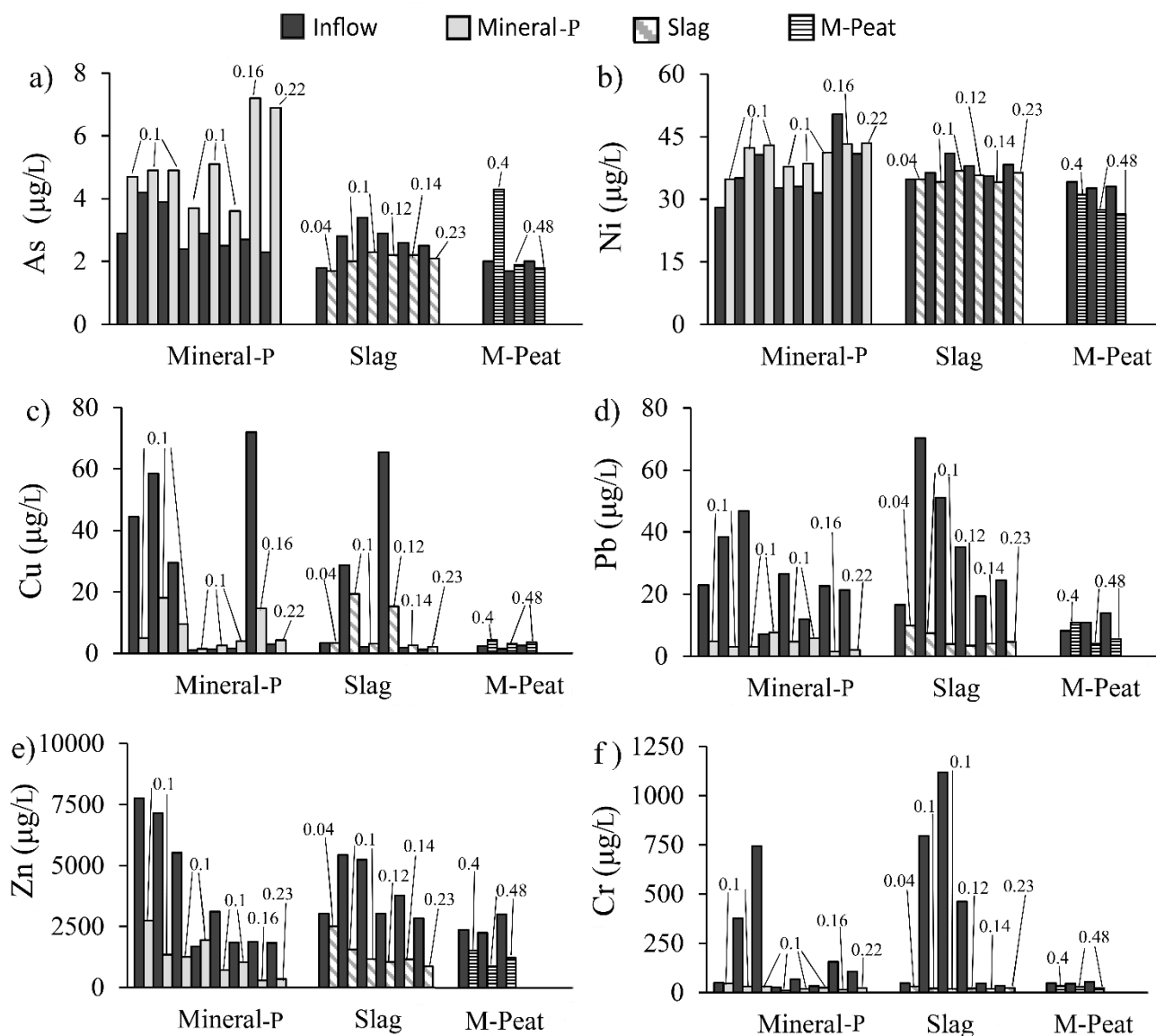
297 Figure 3 – Settling characteristics of the sorbents tested, represented as the removal of turbidity over
 298 time.

299 Based on visual observations, there was a clear distinction in the settling behaviour of the sorbents
 300 tested. The majority of M-Peat particles remained floating (near surface) after mixing stopped. Because
 301 the samples for turbidity measurements were collected below the water surface, most of the floating
 302 particles were not contained in the extracted samples. As the water level in the beaker lowered, some
 303 of the floating particles became attached to the beaker walls and were removed from the suspension,
 304 thus affecting the results obtained (Fig. S1 in Supplementary Material). When Mineral-P was added to

305 water samples, only a small number of Mineral-P particles were observed to float. However, the
306 samples became very turbid after sorbent addition, and this did not change with the allowed
307 sedimentation period (Fig. 3). This indicates that a significant number of small particles remained in
308 suspension, which is corroborated by the increased particulate concentration of all analysed metals
309 found in Mineral-P treated samples during the purification efficiency tests (Table S2).

310 **3.3 Pilot tests**

311 Total concentrations of analysed metals are reported (instead of dissolved concentrations), as they
312 represent the true pollutant load discharged to the environment after treatment. In general, although a
313 few interruptions occurred during the pilot operation (power cut, blockage of dosing pipes, etc.), the
314 experiment can be considered successful. Inflow water quality varied substantially during the pilot
315 experiments (Table 2), and thus direct comparisons of the pollutant removal efficiency of the sorbents
316 tested were not possible. Overall, concentrations were higher in the inflow water during tests with
317 Mineral-P, especially when compared with the concentrations measured during tests with M-Peat (Fig.
318 4). High removal efficiency of Cu, Pb, Zn and Cr was achieved by Mineral-P (Fig. 4c-4f), while
319 leaching of As and to a lesser extent Ni was observed in the majority of collected outflow samples
320 (Fig. 4a and 4b). The Slag material performed well, achieving high removal efficiency of Cu, Pb, Zn
321 and Cr (Fig. 4c-4f), as well as some retention of As and Ni (Fig. 4a and 4b). M-Peat retained Ni, Pb,
322 Zn and Cr satisfactorily, while in a few outflow samples As and Cu concentrations were higher than
323 those found in inflow water (Fig. 4a and 4c). Leaching of metals from M-Peat is unlikely, due to the
324 acid treatment it received during the biomass modification process.



325

326 Figure 4 – (a-f) Total concentrations of different metals in the inflow water and after treatment with
 327 Mineral-P (test time = 120 h), Slag (test time = 165 h) and M-Peat (test time = 21 h). Values above
 328 bars indicate dose of sorbent applied (g/L).

329 The average pH of the inflow water was around 7.0 (st.d. \pm 0.33) during the whole test period (3
 330 sorbents, total of 4 weeks). Addition of Mineral-P and Slag increased the pH of the water substantially
 331 (Fig. S2). The average pH of the outflow water during treatment with Mineral-P was 8.0 (st.d. \pm 0.48)
 332 and 8.3 (st.d. \pm 0.34) during treatment with the Slag product. Addition of M-Peat did not affect water
 333 pH. Measurements of SS concentration were conducted in inflow and outflow samples collected at the
 334 start and end of tests for each sorbent. The SS concentration in inflow samples varied between 4.2-

335 22.9 mg/L. Significantly higher SS concentrations were found in outflow samples treated with M-Peat
336 (62.7-168.2 mg/L) than in samples treated with Mineral-P (4.0-4.2 mg/L) and Slag (0.5-2.7 mg/L).
337 However, it is important to note that the dose of the peat product (0.5 g/L) was substantially higher
338 than that of the other sorbents tested (0.1-0.2 g/L). High SS concentration in the outflow of the
339 sedimentation unit can be due to loss of sorbent particles (the most likely reason here) or to poor
340 retention of particles present in the inflow water or formed during treatment (hydroxide precipitates
341 etc.) (Haas et al., 2019).

342 **3.4 Characterisation of sorbents**

343 Characterisation of fresh and recovered sorbents used during the pilot tests were conducted. The main
344 components of the Mineral-P and Slag materials (fresh and recovered samples) are presented in Table
345 3. Magnesium was the most abundant element (MgO 49.9%) in the Mineral-P sorbent and XRD
346 showed that the main phases present were magnesite, periclase and talc, while the minor phases
347 identified were quartz, chlorite, dolomite, magnetite and hematite. The main component of the Slag
348 material was calcium (CaO 54.7%) and the following phases were identified: calcio-olivine, cuspidine,
349 enstatite, larnite, bredigite, periclase and quartz. There were clear differences between the composition
350 of fresh and recovered materials, e.g. the Mg and Ca concentrations were lower in the recovered
351 Mineral-P and Slag sorbents, respectively, and the concentrations of Cr, Zn and Pb were significantly
352 higher in both recovered products than in their fresh counterparts (Table 3).

353

354 Table 3. Chemical composition of the commercially available Mineral-P sorbent and the Slag material
 355 (fresh and recovered (R) after use for treatment of industrial wastewater).

Analyte	Mineral-P (< 0.125 mm)	Mineral-P R (< 0.125 mm)	Slag (< 5.6 mm)	Slag R (< 5.6 mm)
SiO ₂ , %	17.7	22.3	25.1	23.8
Al ₂ O ₃ , %	1.42	3.1	3.6	5.4
Fe ₂ O ₃ , %	11.6	13.2	0.5	2.1
MnO, %	0.2	0.3	0.3	0.5
MgO, %	49.9	32.7	8.2	11.1
CaO, %	1.1	1.1	54.7	40.6
Na ₂ O, %	0.04	0.1	0.01	0.05
K ₂ O, %	0.04	0.1	0.01	0.09
TiO ₂ , %	0.07	0.10	0.69	0.90
P ₂ O ₅ , %	0.02	0.03	< 0.01	0.02
Cr, ppm	2810	> 10000	6890	> 10000
Co, ppm	97	109	< 1	9
Ni, ppm	1920	1740	90	120
Cu, ppm	20	20	20	30
Zn, ppm	110	> 10000	< 30	> 10000
As, ppm	117	115	< 5	6
Pb, ppm	< 5	91	< 5	45

356 Characterisation of fresh M-Peat was carried out and the results are reported in Gogoi et al. (2018b).
 357 Overall, FTIR showed the presence of hydrogen bonds and hydroxyl groups, as well as aliphatic and
 358 aromatic groups on the sorbent surfaces. FTIR analysis of the recovered M-Peat sample did not show
 359 measurable changes in the structure of the functional groups present in the original material (Fig. S3).

360 4 Discussion

361 *Sorbent performance*

362 The sorption process, and thus purification efficiency, is dependent on e.g. the concentration and type
 363 of ions contained in the water, solution pH, type and dose of sorbent applied etc. (Brown et al., 2000;
 364 Gonzáles and Porovsky, 2014; Leiviskä et al., 2018). Large variations in metal removal efficiency
 365 were observed throughout our study and can be explained to a large extent by the significant variations
 366 in industrial wastewater quality and by the different characteristics of the sorbents tested.

367 Use of the sorbents tested in this study for metal removal in CSTR has not been reported previously,
368 so direct comparison of the results obtained with literature values was not possible. Overall, it can be
369 stated that the M-Peat performed well, achieving good removal of e.g. Zn (50-70%), Ni (30-50%), Pb
370 (60-75%) etc. during laboratory and pilot experiments. Natural and modified peat materials have been
371 found to retain significant amounts of metals (e.g. Ni, Zn, As, Pb, Co etc.) in a number of laboratory-
372 based batch experiment studies (Bulgariu et al., 2011; Gonzales and Porovsky, 2014; Leiviskä et al.,
373 2018). It has been shown that the amount of metals adsorbed depends on the initial solution pH, the
374 concentration and type of ions in solution and the adsorbent dose (Brown et al., 2000; Gonzales and
375 Porovsky, 2014). For example, Gosset et al. (1986) found that for single-metal solutions the maximum
376 adsorption capacity was similar (180 ± 200 mmol/kg) regardless of the metal type, but that the
377 maximum removal rates occurred at different pH values. For Zn, 90% removal was achieved from 0.01
378 M solution at an identified optimum pH of 6.7 (Gosset et al., 1986). These were similar conditions to
379 those prevailing in our laboratory tests with industrial wastewater, apart from the fact that real mixed-
380 metal wastewater was used in our study. In a separate study by our research group in which HCl-
381 treated peat was used for purification of mining-influenced waters in batch experiments, with 15 min
382 contact time, 2 g/L of M-Peat achieved ~50% removal of Ni and As (initial concentration 28.6 and 128
383 $\mu\text{g/L}$, respectively) (Gogoi et al., 2018a). Although the characteristics of the water treated were very
384 different from the samples tested in this study, the mass of e.g. Ni removed per gram of sorbent was
385 very similar to that achieved in our laboratory tests (inflow Ni 42 $\mu\text{g/L}$), which was 0.03-0.04 mg/g
386 M-Peat. The recovery and re-application of used sorbents resulted in higher (>100% for most analysed
387 elements) mass of metal removed per gram of sorbent than for single applications. The combined Ni
388 removal by M-Peat and M-Peat R was 0.08 mg/g. Similarly, removal of Zn by M-Peat was 0.6 mg/g,
389 while the combined removal by M-Peat and M-Peat R was 0.1 mg/g. Thus, re-utilization of recovered
390 sorbents was found to be feasible as satisfactory metal removal efficiencies were achieved during
391 application of 100% recovered products. However, further research is needed to identify optimum ratio

392 of fresh/recovered sorbent required in order for similar metals removal efficiencies achieved by 100%
393 fresh sorbents to be accomplished.

394 The commercially available Mineral-P product showed good performance, as it removed 65-85% of
395 the Zn present in the water samples and it performed similarly in laboratory and pilot tests. In the
396 laboratory experiments, Mineral-P removed 1.8 mg Zn/g of sorbent added (untreated water 0.6 mg
397 Zn/L), while in the pilot tests, the removal rate fluctuated between 4 and 46 mg Zn/g (inflow 1-7 mg
398 Zn/L). The Slag material tested during pilot experiments achieved very good performance, removing
399 65-80% of Zn and 60-80% of Pb from inflow industrial water. Removal of Zn fluctuated between 7.3
400 and 13 mg/g of Slag added (inflow 2-5.5 mg Zn/L). The results obtained were generally better than
401 those achieved by Dimitrova (1996), who tested a similar type of GGBS. In that study, in which batch
402 experiments and mixed-metal solutions of Cu, Ni and Zn (3.5 mM) were used (equilibrium conditions),
403 60%, 46% and 32% removal of Cu, Zn and Ni, respectively, were achieved (Dimitrova, 1996). As a
404 by-product of the metallurgical industry, Slag is an excellent candidate for reducing Zn concentrations
405 from the industry's wastewater flows, as required by environmental permits. The possibility of sorbent
406 recovery and re-application should be investigated, as it can further increase the metal removal
407 capacity of Slag in continuous-flow CSTRs.

408 Leaching of As and Ni occurred from the Mineral-P sorbent in all tests and although not systematic,
409 leaching of Cr and, on fewer occasions, of Cu from the Slag material was observed. Because no
410 threshold concentrations of these elements are mentioned in the environmental permit of the industrial
411 wastewater provider, Finnish drinking water quality standards (D 1352/2015) and environmental
412 quality standards (AA-EQS, 2013/39/EU) were used to assess the magnitude of the concentrations
413 discharged. These showed that, the average As concentrations in Mineral-P treated water samples
414 (laboratory and pilot) were under the Finnish drinking water quality limit (10 µg/L), while the Ni
415 concentrations (40-55 µg/L, of which 80-90% was contained in inflow water) were above the limit (20
416 µg/L). The Cr and Cu concentrations in samples treated with Slag were all under the drinking water

standards limits (50 µg/L and 2 mg/L respectively). From the metals studied, Cd, Pb and Ni received limit values for “Annual Average Environmental Quality Standard” (AA-EQS) in the directive (2013/39/EU). The industrial plant where pilot experiments were conducted discharges into the Baltic Sea, for costal waters AA-EQS values are provide for dissolved concentrations of discharging contaminants. The average Cd concentrations in raw and treated industrial wastewater (laboratory and pilot) did not exceed the AA-EQS limit of 0.2 µg/L (Fig. 2 and Tables S2 and S3 supplementary material). The average Pb concentration in the industrial wastewater exceed the AA-EQS limit (1.3 µg/L) before treatment. However, treatment with all sorbents resulted in Pb concentrations lower than AA-EQS limit (1.3 µg/L, Fig. 2 Tables S2 and S3). The average Ni concentration exceed the AA-EQS limit (8.6 µg/L) before and after treatment with all sorbents tested. In general, the concentrations of metals leached from Mineral-P and Slag were low. However, they can still result in undesired loads of these metals to the receiving environment. Use of metal-containing sorbents for the treatment of dilute streams should thus be carefully assessed.

Settling characteristics of sorbents particles

The settling properties of the sorbent particles dictate the retention time needed in the sedimentation unit for successful solid/liquid separation (removal of the sorbent material) and effective purification of the water. Thus, they have a direct impact on the cost-effectiveness and suitability of the sorbent. The sedimentation time provided in this study was 60 min during pilot experiments and 30 min during laboratory tests. It appeared that the longer sedimentation time provided in the pilot system improved the retention of sorbent particles compared with results obtained in the laboratory-scale tests (Table S2). Addition of the sorbents as a slurry during pilot experiments reduced the substantial floating of M-Peat particles observed during laboratory experiments. However, significant loss of M-Peat particles still occurred during pilot tests (SS concentration in outflow 62.7-168.2 mg/L). The loss of sorbent particles can result in an increased impact on the receiving environment, as the SS load increases and previously adsorbed pollutants can leach under new conditions.

442 Modifications to the design of the sedimentation units (e.g. increased retention time, etc.) have the
443 potential for decreasing sorbent particle losses. A rough estimation of peat particle settling velocity
444 was made using Stoke's law, the particle size range applied (90-250 μm) and the density of the M-Peat
445 material tested (1.1 g/cm^3). The estimated settling velocity was then used to estimate the settling
446 distance travelled by the sorbent particles in the retention time provided (60 min). Settling distance
447 was estimated to range from 17 cm (90 μm particles) to 45 cm (250 μm particles). Therefore, the
448 smallest particles contained in the material tested would require at least double the retention time (120
449 min) for effective removal. However, longer retention times require larger sedimentation units, which
450 results in increased costs. Successful use of chemical flocculants to improve peat particle settling has
451 been reported (Leiviskä et al., 2018). Granulation of peat has been used successfully to produce a
452 sorption material of variable particle size to be used in filter-type systems (Eger et al., 2015). Small-
453 sized granules could improve the solid/liquid separation stage of CSTR followed by sedimentation.
454 The use of CSTR coupled with filter units could be a feasible option (Reddad et al., 2003). As peat is
455 a widely available biodegradable material in Finland, where it is used in energy production, the use of
456 peat for metal removal from diluted streams could represent an additional utilisation step between peat
457 extraction and incineration, therefore increasing its inherent value.

458 *Metal removal mechanisms*

459 Although metal removal mechanisms were not studied, a few statements can be made on the results
460 obtained. Metal removal mechanisms are affected by a number of factors such as pH, chemical
461 composition of sorbent materials and metal speciation. Mineral-P and the Slag materials were a
462 mixture of different oxide minerals; it is known that functional groups on the surface of minerals are
463 able to bind metal cations in a mechanism that is strongly pH dependent. In general, cation adsorption
464 increases with increasing pH due to higher number of negatively charged species on the surface of
465 mineral-based materials (~~Plumlee and Logsdon, eds., 1999~~Smith, 1997). In general, addition of
466 Mineral-P (laboratory and pilot) and Slag (pilot) had considerable effects on the water pH. This was

467 due to the dissolution of alkaline compounds (e.g. Ca, Mg etc.) from the sorbents, as confirmed by the
468 lower concentration found in the recovered materials (Table 3). It can be assumed that e.g. Zn removal
469 by Mineral-P and Slag was due (at least in part) to precipitation in the form of hydroxide precipitates
470 (Zn(OH)_2), as formation of such precipitates has been reported to begin at the pH range between 5 and
471 7 (Balintova et al., 2012). The characterisation results for the recovered sorbents during the pilot
472 experiments confirmed that the Zn content was higher in the recovered mineral sorbents (Table 3), but
473 the exact mechanism was not revealed, partly due to the complex mixture of minerals found in the
474 studied mineral sorbents. The pH range for optimum Ni sorption has been found to be around 5-6,
475 while at alkaline pH values ($\text{pH} > 7.5$) Ni starts to precipitate as Ni(OH)_2 (Bartczak et al., 2017). As
476 the Ni concentrations in untreated water samples were very low during our study ($< 100 \mu\text{g/L}$),
477 occurrence of Ni(OH)_2 precipitation although unlikely can not be discarded (Haas et al., 2019). As
478 Mineral-P and Slag included Ni in their composition (Table 3), dissolution of Ni into solution possibly
479 occurred which, among other factors, might have resulted in the low Ni removal efficiency achieved.
480 The addition of M-Peat did not affect water pH, it can thus be assumed that physical-chemical sorption
481 processes were responsible for the removal of metal ions from water. Removal was most likely due to
482 interactions between functional groups with metals ions and other polar molecules in the biosorbents
483 surface, which occur through different processes such as surface adsorption, complexation, etc. but
484 mostly as ion exchange reactions (Brown et al., 2000; Bulgariu et al., 2011; Kumar et al., 2016).

485 **5 Conclusions**

486 Chemically treated peat (HCl) a commercially available mineral sorbent and a slag (GGBS, by-product
487 of stainless steel production) were tested for their efficiency in removal of metals from industrial
488 wastewater samples (metallurgy). The suitability of the sorbents for application in a continuous stirred
489 tank reactor (CSTR) coupled with a sedimentation unit was assessed in in two experimental phases, i)
490 laboratory experiments (jar-test, proof of concept for CSTR) and pilot-scale experiments simulating a
491 continuous-flow CSTR. Based on the results obtained, the following conclusions can be drawn:

- 492 - Overall, higher metal removal was achieved from samples with higher initial metal
493 concentrations. As the concentration of ions in the wastewater used varied significantly and
494 had a direct impact on sorption and other retention processes, direct comparison of the pollutant
495 removal efficiency of the sorbents tested was not possible.
- 496 - M-Peat performed well, achieving good removal of Zn (50-70%) and Ni (30-50%) during
497 laboratory and pilot experiments.
- 498 - The commercially available Mineral-P product showed good performance, removing 65-85%
499 of Zn present in the water samples and performing similarly in laboratory and pilot tests.
500 However, leaching of As and Ni in low concentrations occurred from the sorbent in all tests.
- 501 - The ground granular blast furnace Slag (GGBS) material tested (pilot) achieved very good
502 performance, removing 65-80% of Zn and 60-80% of Pb from industrial water. As a by-product
503 of the same industry (metallurgical) that produces the wastewater tested, the material is an
504 excellent candidate for reducing Zn concentrations, as required by the company's
505 environmental permit. However, leaching of Cr and, on fewer occasions, of Cu was observed
506 from this material.
- 507 - Use of the sorbents tested in a continuous-flow CSTR coupled with a sedimentation unit is a
508 feasible option and should be explored further. However, the poor settling characteristics of M-
509 Peat observed during the experiments (laboratory and pilot) can restrict its use in this type of
510 system.

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521

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