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1   **Influence of pH adjustment on chemical purification efficiency: Neutralisation of acidic effluent**

2   **from chemically treated runoff water using industrial by-products**

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10   **Abstract:**

11   Chemical treatment has long been considered best available technology for purification of humic natural

12   waters, e.g. for treatment of peat extraction runoff. Metal salts of iron are currently used in several

13   treatment facilities in Finland. However, variations in runoff water quality and lack of refinement of

14   process parameters have led to fluctuations in purification efficiency, low pH and high metal concentration

15   in treated waters. This study investigated the suitability of a range of calcium-based alkaline products

16   (including by-products of the paper, cement and mineral industries) for neutralisation of chemically treated

17   runoff water (SUVA = 3.3). The influence of the time of pH adjustment relative to time of coagulant

18   addition and whether observed influences were dependent on the physical form of the coagulant were

19   evaluated. The best performing pH-adjusting products were CKD (CaO and SiO_2) and MAHT ($Ca(OH)_2$,

20    $CaCO_3$ and CaO), by-products of the cement and paper industry, respectively. Time of pH adjustment in

21   relation to time of coagulation addition had a significant influence on purification efficiency, especially

22   when solid $Fe_2(SO_4)_3$ was applied. Adjustment of pH at 30 s before coagulant dosing resulted in a negative

23   effect on treatment results. Furthermore, dosing of $Ca(OH)_2$ prior to addition of coagulant did not give any

24   measurable benefits in floc formation for the pH levels tested. For effective removal of DOC and SS,

25   suggested points of pH adjustment are during the flocculation stage or at the outlet of sedimentation,

26   particularly if solid coagulants are applied.

27   **Keywords:** Coagulation pH, neutralisation products, humic waters

1. Introduction

28

29   Chemical purification is considered by the Finnish environmental authorities to be one of the best available

30   technologies for treatment of peat extraction runoff (Finnish Ministry of the Environment, 2015).

31   However, due to cost-related issues, small-scale and low-tech chemical treatment facilities are normally

32   implemented, where solid metal salt coagulants are often dosed without pre-dissolution

33   (Turveteollisuusliitto, 2010; Finnish Environmental Institute, 2015). This has resulted in a lack of control

34   of key process parameters such as mixing and coagulant dosage, which has led to fluctuations in

35   purification efficiency, increased acidity (pH<5) and elevated metal concentration in the purified water

36   (Heiderscheidt et al., 2013; Finnish Environmental Institute, 2015). Optimisation measures are therefore

37   required to improve process performance and increase the reliability of the method, thereby decreasing the

38   discharge of acidic and metal-rich effluent into the environment.

39   Chemical treatment (coagulation/flocculation) is a globally widely applied method for purification of

40   water and wastewaters from various sources. Metal salts of iron and aluminium are commonly used as

41   coagulant agents; they are cost-effective products which are particularly efficient in the removal of

42   suspended solids (SS), dissolved organic carbon (DOC), phosphorus etc. (Bratby, 2006). In coagulation

43   by metal salt addition, the pH at which coagulation takes place is a critical factor influencing process

44   efficiency. It affects the properties and characteristics of pollutant substances and the metal hydrolysis

45   species formed when the coagulant is added to the water (Duan and Gregory, 2003; Bratby, 2006; Slavik

46   et al., 2012; Feng et al., 2015). Because the coagulant interacts with dissolved, colloidal and particulate

47   matter via different mechanisms (e.g. complexing, adsorption, neutralisation, entrapment etc.), the

48   optimum pH conditions for effective purification change according to the quality of the water, removal

49   requirements and the type and dose of coagulant applied (Duan and Gregory, 2003, Matilainen et al., 2010;

50   Slavik et al., 2012). An important characteristic of metal salts is that they react with the available alkalinity

51   of the water, thus depressing the water pH. Adjustment of pH or addition of alkalinity may be necessary

52   to regulate the coagulation pH to an optimum range or to increase the pH after treatment, in order to comply

53   with distribution or discharge limits. Moreover, in the treatment of low turbidity and humic waters, pH

54   adjustment via lime-based products can be used to enhance the purification process by promoting the

55   formation of metal hydroxide precipitates and co-precipitation reactions between the coagulant and humic

56   acids (Duan et al., 2012) as well as improving the flocculation process by providing nuclei sites for floc

57   formation (Gregor et al., 1997). The adjustment of pH is therefore an important stage of chemical treatment

58   and its influence on purification efficiency depends not only on the coagulant agent applied, but also on

59   the type of neutralisation agent added and the time of addition (Slavik et al., 2012). A number of studies

60   have examined the effect of pH on coagulation and report benefits and drawbacks of pH adjustment before

61 or after coagulant addition, as well as the type of neutralisation agent used (Gregor et al., 1997; Yan et al.,

62 2008; Slavik et al., 2012). However, such studies normally use synthetic solutions targeting removal of

63 single pollutants (e.g. DOC, SS etc.) and compare limited points of pH adjustment, Furthermore, studies

64 on the use of solid coagulants are scarce. Therefore, the aim of this work was to decrease the existing lack

65 of information regarding the influence of pH adjustment and of the time and type of neutralisation agent

66 addition on purification efficiency, especially when solid coagulants are applied.

67 In general, calcium hydroxide Ca(OH)$_2$, calcium carbonate (CaCO$_3$) and sodium hydroxide (NaOH) are

68 common alkaline materials used in neutralisation of acidic effluents or as providers of alkalinity for the

69 coagulation process. However, while NaOH or Ca(OH)$_2$ are often utilised in water and wastewater

70 treatment due to low required dosage and low costs, they do not provide residual alkalinity (buffering

71 capacity), which makes fine pH control difficult. In the neutralisation of industrial wastewaters and acidic

72 runoff, e.g. from acid sulphide soils and mining areas, CaCO$_3$ (limestone) is normally used. Although

73 longer retention times are required, due to slower reactions, the use of CaCO$_3$ eliminates the risk of over-

74 neutralisation (pH < 8.5) and provides residual alkalinity (Stumm and Morgan, 1996). An important aspect

75 is that the need for pH neutralisation increases the costs and overall environmental impacts related to

76 chemical purification. Lime-based products (calcium-containing inorganic materials) are utilised in the

77 production processes of several industries (e.g. paper, cement, mineral etc.) and are often contained in by-

78 products generated by these industries. The potential use of these by-products as neutralisation agents in

79 water and wastewater treatment processes has not yet been fully explored. The use of industrial by-

80 products can decrease costs while supporting the sustainable use of natural resources and the principle of

81 a circular economy, leading to the development of more sustainable water and wastewater purification

82 methods (European Commission, 2015).

83 The aim of this work was thus to evaluate how pH adjustment affected the chemical purification of peat

84 extraction runoff water (typically humic and low alkalinity). The first objective was to determine the

85 influence of time of pH adjustment (multiple points before and after coagulant addition) and type of pH-

86 adjusting product (Ca(OH)$_2$, CaCO$_3$, CaO, etc.) on purification efficiency. A second objective was to

87 identify whether the influence of pH adjustment was dependent on the physical form (solid or solution) of

88 the coagulant used (Fe$_2$(SO$_4$)$_3$). A third objective was to determine the suitability of a wide range of

89 neutralising materials (including by-products of the paper, cement and mineral industries) for

90 neutralisation of peat extraction runoff water submitted for chemical treatment.

2. Materials and methods

Peat extraction runoff water was obtained from a field site and the jar test methodology was applied to simulate the chemical purification process. Experimental procedures were designed to evaluate: 1) the dose of coagulant (solid and liquid) required for effective purification; 2) the dose of pH-adjusting products required to achieve a final water pH of 5.5; 3) the influence of pH adjustment on purification results; and 4) the influence on purification efficiency of time of pH adjustment in relation to time of coagulant addition.

2.1 Characteristics of water and tested chemicals

Runoff water (400 L) was collected from a peat extraction site managed by Vapo Oy located in Vaala (E: 3475877, N: 7138725), northern Finland. Periodic water quality analyses were conducted during the 6-week test period to monitor any changes in water characteristics (Table 1). Ferric sulphate ($Fe_2(SO_4)_3$) was the coagulant agent selected, based on results from a previous study (Heiderscheidt et al., 2013) and the fact that it is the coagulant normally applied in existing treatment facilities in Finland. A commercial-grade solid product (Kemira Oyj, Kemwater; 90% purity) was dosed in its original solid form and as a stock solution (10 g/L). Purification tests were performed using the six-jar (1 L) programmable paddle stirrer jar test equipment Flocculator 2000 (Kemira Kemwater). The pH was adjusted to a final value of around 5.5 by addition of calcium-based products, the characteristics of which are listed in Tables 2 and 3.

Water quality analyses were conducted on samples before and after purification and pH adjustment. The analyses, which were performed by a certified laboratory (using SFS-EN and ISO standard methods) determined: Total phosphorus (tot-P, SFS-EN ISO 6878:2004, detection limit >0.5 µg/L), phosphorus (P, ICP-OS: ISO 11885:2007, detection limit >50 µg/L), phosphate-phosphorus (PO_4-P), ammonium nitrogen (NH_4-N), alkalinity (Alk), acidity (Acid) and sulphate (SO_4). Selected samples were also analysed for concentrations of the following elements: Al, As, Ba, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Na, Sr, S, Ti, U, V and Zn.

Water quality analyses were also performed at the in-house laboratory using standard methods to determine: Dissolved organic carbon (DOC, SFS-EN 1484:1997, Sievers 900 Portable TOC Analyzer, 0.45 µm filtration); suspended solids (SS; (GFC) SFS-EN 872:2005); turbidity (EN 27027:1994; Hach Ratio/XR Turbidity meter), colour (ISO 7887:1994; Lovibond Nessleriser Daylight 2000); and pH (SFS-EN 13037:1994; WTW Universal meter Multiline P4 Sensor: WTW Electrode Sentix 81). Analysis of UV absorbance at 254 nm (UV_{254} abs) was conducted using a UV 1800 spectrophotometer (Shimadzu, Japan) following the manufacturer's instructions (filtration of samples was not performed). Specific UV

absorbance (SUVA, L/mg-m) was determined by dividing the measured UV_{254} abs. by the DOC content of the samples. Charge quantity (eq/L) measurements were performed using the Mütek particle charge detector PCD 03 PH (Mütek Analytic GmbH, Germany) following the equipment manual. The method measures the total surface charge contained in the suspension using the streaming current principle. The samples were titrated using either cationic or anionic polyelectrolytes (0.001 eq/L) until the charge of the sample was neutralised. The Cq value (eq/L) of the sample was then determined based on the concentration and amount of polymer required for neutralisation of 10-mL samples.

Table 1 – Water quality characteristics of peat extraction runoff water used in tests.

Water quality parameters	Mean ± Std. dev.	Number of analyses n
DOC (mg/L)	23.5 ± 1.8	5
Colour (mg Pt/L)	339.0 ± 32.7	7
SS (mg/L)	14.0 ± 2.4	5
Turbidity (NTU)	21.3 ± 2.6	7
tot-P (µg/L)	100 ± 8	3
PO_4-P (µg/L)	43 ± 16	3
NH4-N (mg/L)	186.7 ± 9.4	3
Fe (mg/L)	6.9 ± 0.1	3
Al (µg/L)	217 ± 5	3
Alkalinity (mmol/L)	0.61 ± 0.01	3
Acidity (mmol/L)	0.12 ± 0.02	3
Cq (µeq/L)	-83.5 ± 5.0	4
SUVA (L/mg-m)	3.27 ± 0.11	3
pH	6.2 – 6.8	7

The pH-adjusting products tested comprised (Table 2): 1) FC7, a product of the mineral industry normally used as a filler in paints and coatings, adhesives, plastics and rubber compounds, but tested here in a new application; 2) cement kiln dust (CKD), a by-product of the cement industry. It is a fine, powdery material, the composition of which depends on the location within the dust collection system, the type of operation, the dust collection facility and the type of fuel used and thus must be evaluated on a plant-by-plant basis; 3) lime kiln dust (LKD), a by-product of the lime industry; 4) multicone kiln dust (MKD), also a by-product of the lime industry that mostly comprises dry collected kiln dust; 5) paper bleaching sludge (Pmud), a by-product of paper industry mainly composed of $CaCO_3$ (up to 85%) depending on the process efficiency, and as a primary sludge it contains a high amount of cellulose fibres; and 6) Mahtikalkki (MAHT), the commercial name given to a by-product of the paper industry in Finland. It is a generated in the precipitated calcium carbonate process (PCC) and contains a mixture of calcium components, with low residual contaminants and fibres. Analytical quality calcium hydroxide ($Ca(OH)_2$; Merk KGaA, GER) was also included, as a reference product..

143 **Table 2** – Characteristics of calcium-based products tested for pH adjustment in the treatment of peat
144 extraction runoff by coagulation.

Producer Type of material	Product name	Composition	Particle size distribution original	Pre-treatment	Particle size distribution after pre-treatment
Nordkalk, Lappeenranta, FIN Product of mineral industry	FC7	$CaCO_3$ > 98% Other minerals < 2%	98% < 30 μm 50% < 7 μm	Drying	98% < 30 μm 50% < 7 μm
Nordkalk, Tytyri, FIN By-product of mineral industry	LKD	$CaCO_3$ 58.5% CaO 27.2% Other minerals 14.3%	91,2% < 125 μm 52,5% < 32 μm	Drying	91.2% < 125 μm 52.5% < 32 μm
Nordkalk, FIN By-product of mineral industry	MKD	$CaCO_3$ 95% Other minerals 5%	99,1% < 32 μm 31,2% < 4 μm	Drying	99.1% < 32 μm 31.2% < 4 μm
Finnsementti, Espoo, FIN By-product of cement industry	CKD	CaO 65% SiO_2 22%	100% < 1mm 82% < 125 μm	Drying	100% < 1mm 82% < 125 μm
Storaenso Imatra, FIN By-product of paper industry	MAHT	CaO, $Ca(OH)_2$, $CaCO_3$	2-12 mm	Drying Grinding	100% < 1 mm 57% < 0.5 mm
Storaenso, Kemi, FIN By-product of paper industry	Pmud	$CaCO_3$ (+ cellulose fibres) with at least 30% Ca	2-30 mm (fibre agglomerate)	Drying Grinding	91.3% < 1 mm 72.4% < 0.5 mm
Merk KGaA, GER Analytical quality	Calcium hydroxide $(Ca(OH)_2)$	$Ca(OH)_2$	Not measured (fine powder)	Drying	Not sieved (fine powder)

145 The reported properties of the pH-adjusting products tested consist of information provided by the
146 suppliers/producers, in-house measurements (Table 2) and data on elemental composition determined
147 using the X-ray fluorescence (XRF) method (Table 3) by a certified laboratory. All products were pre-
148 treated before elemental analysis and purification tests. This involved drying at 105 ºC for 2 hours before
149 further treatment which included grinding or blending and sieving for particle size determination (two
150 replicates, Table 2). A Bruker AXS S4 Pioneer XRF spectrometer was used to determine the elemental
151 composition of pre-treated samples. For XRF analysis, 13.16 g of sample was mixed with 0.84 g of C-
152 wax. A WC/Co mortar HERZOG pulverising mill was used to obtain a homogeneous dispersion and
153 uniform particle size of the resulting mixture (sorbent and C-wax). Pressed pellets for XRF analysis were
154 prepared from the mixture (7-8 g) using boric acid as a binder and applying a hydraulic pressure of 10 ton
155 to compress the sample.

156

Table 3 – Elemental composition (wt.-%) of the six pH-adjusting by-products tested, according to X-ray fluorescence (XRF) analysis (for complete XRF results, see Table S1 in Supplementary Material).

Product	CaO	SiO$_2$	FeO	K$_2$O	Na$_2$O	MgO	Al$_2$O$_3$	P$_2$O$_5$
FC7	79.0	1.2	0.1	0.0	0.0	0.6	0.0	0.4
LKD	67.9	9.4	1.6	0.8	0.3	1.6	2.6	0.4
MKD	75.2	1.0	0.1	0.0	0.9	0.8	0.0	3.7
CKD	58.0	12.3	1.9	5.4	1.4	1.6	2.2	0.3
MAHT	79.6	1.7	0.2	0.1	0.0	0.8	0.0	0.4
Pmud	74.5	0.8	0.2	0.0	0.0	0.5	0.1	0.4

2.2 Experimental procedure

A suspension (10% in mass) of each of the pH-adjusting products tested was created by mixing a suitable amount of product with deionised water in a plastic container. The container was then transferred to rotational shaking equipment and the suspension was mixed (40 rpm) for 12 hours. At the time of application, the suspension was transferred to a glass beaker mounted on a magnetic mixer, allowing full homogenisation prior to dosing, which was carried out with a volumetric pipette.

Experimental procedures were based on the jar test methodology and divided into four phases as follows:

Phase 1) Evaluation of required coagulant dose for effective purification: Increasing doses of $Fe_2(SO_4)_3$ (solid and stock solution) were added to 1 L samples of runoff water. Mixing parameters applied: 300 rpm for 60 s followed by 50 rpm for 25 min and 30 min of sedimentation. Measurements of colour, turbidity, pH and Cq were performed on the purified samples. The dose that provided the best removal of colour and turbidity (>90%) was identified as the optimum dose for the coagulant and reported in mg of product per litre of water (two replicates).

Phase 2) Evaluation of required dose of pH-adjusting products for a final water pH of 5.5: The optimum dose of solid or pre-dissolved $(Fe_2(SO_4)_3)$ coagulant was added to 1 L water samples while the pH of the water was continuously monitored. This was followed by 60 s of rapid mixing and 5 min of slow mixing before an increasing dose of individual pH-adjusting products was applied to each sample until a pH of 5.5 was achieved (two replicates). The dose of neutralisation products that resulted in pH 5.5 was identified as the optimum dose of the product and reported in mg of product per litre of water.

Phase 3) According to previous studies (Heiderscheidt et al., 2016), effective purification of typically humic and low alkalinity runoff water requires lower coagulant doses at acidic pH levels (4-5) than in neutral conditions. The recommendation is thus that pH adjustment be conducted after the coagulation process, so that discharge limits (pH $\geq$ 5) can be met. Based on this, in evaluation of the influence of pH adjustment on purification results, the selected point of pH adjustment in this phase was 15 min inside the flocculation stage (total of 25 min). This allowed the coagulation to be completed and the flocculation

184 process to be well underway, while also providing mixing for dispersion of the pH-adjusting product. The

185 procedure followed was: The optimum dose of solid $Fe_2(SO_4)_3$ was added to 1 L samples and mixing was

186 introduced as described in phase 1. For samples where pH adjustment was not conducted, a 400 mL sample

187 of the supernatant water was collected at the end of the sedimentation period for analysis (two replicates).

188 For samples where pH adjustment was conducted, the required dose of individual pH-adjusting products

189 was applied after 15 min of slow mixing and a 400 mL sample of the supernatant water was collected at

190 the end of sedimentation for analysis (two replicates). To evaluate the amount of sludge produced a similar

191 procedure was followed, but samples were not allowed to sediment. The total volume (1 L) of the treated

192 sample was filtered once the slow mixing stage of the purification process ended. The standard method

193 (GFC) SFS-EN 872:2005 was used for determination of SS in the sample and the value obtained was taken

194 as total suspended solids (TSS) and used as an indicator of the amount of sediment produced during the

195 purification process. Based on product availability, status (by-product/product), composition ($Ca(OH)_2$,

196 $CaCO_3$ or mixed) and required dose and purification results, three of the pH-adjusting products tested were

197 selected for the next phase of experiments. Priority was given to the $CaCO_3$-based by-product MKD over

198 the material FC7, which is used in the construction sector and for which a new application was evaluated

199 in this study.

200 Phase 4) Evaluation of the influence of time of pH adjustment on purification efficiency: Based on the

201 structure and organisation (dosing equipment, hydraulic conditions, process units etc.) of existing

202 treatment facilities, practical points of pH adjustment or procedures for dosing of pH-adjusting products

203 in relation to coagulant addition were selected as follows: a) -30 seconds (30 s before $Fe_2(SO_4)_3$ addition);

204 b) +30 seconds (30 s after ($Fe_2(SO_4)_3$) addition); c) + 11 minutes (11 min after $Fe_2(SO_4)_3$ addition, 10 min

205 inside the slow mixing stage); d) post-sedimentation (post-sed), emulating the situation where the pH-

206 adjusting product is added at the outflow of the sedimentation basin. The identified optimum dosage of

207 $Fe_2(SO_4)_3$ was added to 1 L samples and mixing was introduced as described in phase 1. For procedures

208 a-c, pH-adjusting product was then added according to the description (-30 s, +30 s and +11 min). At the

209 end of sedimentation, a 400 mL sample of the supernatant water was collected for analysis. For procedure

210 d, at the end of the sedimentation period a 500 mL sample of the supernatant water was transferred to a

211 second beaker, where the pH-adjusting product was added and the following mixing applied: 10 s of fast

212 mixing (300 rpm) followed by 2 min of slow mixing (50 rpm) and 5 min of sedimentation. The supernatant

213 water (250 mL) was collected for analysis. Two replicates of procedures a-d) were performed, as well as

214 two replicates of a run where pH-adjusting products were not added during the purification process.

215 Procedures a-c were performed for $Fe_2(SO_4)_3$ in solid and pre-dissolved form, while procedure d) was only

216　performed for solid $Fe_2(SO_4)_3$. An extra replicate of procedures a-d was conducted in which the pH of the

217　samples was continuously monitored and recorded at 1-s intervals using an YSI 6600 V2 probe.

3. Results

3.1 Required dose of coagulant and pH adjusting product and overall purification efficiency

220　On evaluating the dose of solid/pre-dissolved $Fe_2(SO_4)$ required for effective purification (Fig. 1), it was

221　found that, when doses lower than the optimum were applied, sharp increases in turbidity and colour values

222　were only observed in samples treated with solid $Fe_2(SO_4)$ (Fig. 1a). Comparative doses of solid coagulant

223　were also less effective than pre-dissolved coagulant in neutralisation of surface charges (Cq) contained

224　in solution at a particular pH level (Fig. 1c). The optimum dose of the coagulant identified for efficient

225　removal (90%) of colour and turbidity was 80 mg/L for solid $Fe_2(SO_4)$ (Fig. 1a) and 75 mg/L for pre-

226　dissolved $Fe_2(SO_4)$ (Fig. 1b).

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228

229　**Figure 1** – Removal of colour and turbidity and resulting water pH with increasing dose of coagulant (1a

230　and 1b) and charge quantity (Cq) with increasing dose of coagulant (1c). Minimum and maximum values

231　of replicates indicated by error bars.

232 Samples treated with the optimum dose of solid and pre-dissolved coagulant had pH values around 4.5

233 (Fig. 1a and 1b). Thus, pH adjustment of purified water would be necessary to meet the discharge limits

234 and avoid acidification of receiving water bodies. For an initial assessment of the influence of pH

235 adjustment on overall purification efficiency, solid $Fe_2(SO_4)_3$ was the coagulant used and pH adjustment

236 was performed 15 minutes inside the flocculation period (total of 25 min).

237 All pH-adjusting products tested (Table 2) proved capable of increasing the pH of the water to 5-5-6.5

238 within the provided retention time (10 min of mixing plus 30 min sedimentation). The dose required for

239 the analytical quality $Ca(OH)_2$ was 8 mg/L, while the other products tested required doses between 20 and

240 50 mg/L to achieve the desired pH value. Higher residual DOC concentrations (15-30%) were found in

241 samples where pH adjustment took place, with the highest residual observed in samples where the by-

242 product Pmud was applied (Table 4). Adjustment of pH during the flocculation stage appeared not to

243 influence the properties and settling characteristics of the flocs formed. Similar SS concentrations were

244 found in all treated samples at the end of the sedimentation period, despite the addition of pH-adjusting

245 products mid-way through flocculation (Table 4). The only exception was Pmud samples, which displayed

246 a significant increase in SS concentration compared with samples treated with solid $Fe_2(SO_4)_3$

247 exclusively.

248 **Table 4** – Dose of pH-adjusting products applied for neutralisation of samples treated with solid

249 $Fe_2(SO_4)_3$, mean residual concentration of selected substances and final water pH (mean ± maximum and

250 minimum values of replicates).

Added chemical	Dosage (mg/L)	DOC (mg/L)	SS (mg/L)	*TSS (mg/L)	P (µg/L)	S (mg/L)	Fe (mg/L)	Ca (mg/L)	pH
Untreated water	0	24.0 ± 2.1	14.0 ± 2.6	--	74 ± 0	0.7 ± 0.1	6.9 ± 0.1	6.1 ± 0.0	6.5 ± 0.3
$Fe_2(SO_4)_3$	80	7.5 ± 0.1	3.3 ± 1.1	77.0	<50**	14.5 ± 1.0	1.6 ± 0.1	6.1 ± 0.1	4.3 ± 0.1
$Fe_2(SO_4)_3$ + $Ca(OH)_2$	80+8	8.7 ± 0.3	2.0 ± 0.7	78.0	<50**	15.0 ± 1.0	1.8 ± 0.0	10.3 ± 0.2	5.8 ± 0.1
$Fe_2(SO_4)_3$ + MKD	80+40	9.1 ± 0.3	3.3 ± 2.0	93.1	80 ± 20	15.0 ± 0.0	1.3 ± 0.0	12.9 ± 0.3	6.1 ± 0.0
$Fe_2(SO_4)_3$ + FC7	80+30	8.6 ± 0.5	2.8 ± 1.9	85.6	<50**	15.0 ± 0.0	1.4 ± 0.1	12.0 ± 0.1	5.8 ± 0.1
$Fe_2(SO_4)_3$ + MAHT	80+40	9.2 ± 0.4	3.2 ± 1.2	81.4	<50**	14.5 ± 1.0	1.8 ± 0.1	11.3 ± 0.1	5.8 ± 0.1
$Fe_2(SO_4)_3$ + LKD	80+30	9.2 ± 0.1	4.0 ± 1.3	93.0	<50**	15.0 ± 0.0	2.5 ± 0.3	11.5 ± 0.1	6.0 ± 0.0
$Fe_2(SO_4)_3$ + CKD	80+23	9.2 ± 0.0	3.7 ± 1.7	82.4	<50**	14.5 ± 1.0	1.9 ± 0.0	11.5 ± 0.1	6.0 ± 0.1
$Fe_2(SO_4)_3$ + Pmud	80+50	9.6 ± 0.3	7.3 ± 2.6	112.9	<50**	14.5 ± 1.0	1.7 ± 0.2	13.3 ± 0.2	6.3 ± 0.0

251 *Total suspended solids, i.e. amount of solids contained in the water after addition of chemicals, but before

252 sedimentation. **Detection limit.

253 The TSS values (Table 4) show the amount of solids in suspension at the end of the flocculation process,

254 i.e. they give an indication of the amount of sediment that will accumulate at the bottom of the

255 sedimentation basin, which has a clear effect on cost-effectiveness. The TSS concentration found in

256 samples to which analytical quality $Ca(OH)_2$ was added was very similar to the concentration found in

257 samples treated only with $Fe_2(SO_4)_3$. The increased TSS concentrations observed in samples treated with

258 the other pH-adjusting products were most likely the result of presence of non-reactive material or

259 impurities in their composition (e.g. Pmud and LKD) and of increased formation of metal hydroxides and

260 CaCO3 precipitates (e.g. FC7 and MKD) after pH adjustment. Satisfactory removal of phosphorus was

261 obtained for all treatment combinations apart from samples treated with Fe2(SO4)3 + MKD, where no

262 removal or an increase in phosphorus concentration was observed. Results of XRF analysis showed that

263 phosphorus compounds made up around 1.8% of MKD composition (Table 3), confirming that the increase

264 in phosphorus concentration in MKD-treated samples was due to release of phosphorus from the product

265 itself. Elemental analysis conducted on raw water and treated water samples (Table S2 in Supplementary

266 Material) showed a slight increase in compounds such as Ni, Co and S in all treated samples. These can

267 be mostly attributed to the coagulant addition (composition and impurities). Samples treated with FC7 and

268 CKD also showed a small increase in Sr and Cu concentrations.

269 **3.2 Influence of time of pH adjustment on purification efficiency**

270 The influence of time of pH adjustment in relation to time of addition of the coagulant on the overall

271 purification efficiency was evaluated. Whether the influence of pH adjustment was dependent on the

272 physical form (solid or solution) of the coagulant applied was also studied.

273 **3.2.1 Coagulation with solid Fe$_2$(SO$_4$)$_3$**

274 Three pH-adjusting products were selected based on their composition, status, availability and overall

275 efficiency: analytical quality Ca(OH)2, the mixed composition by-product MAHT (Ca(OH)2, CaCO3 and

276 CaO) and the CaCO3 based by-product MKD. At the time of product selection, results of outsourced water

277 quality analysis from the first phase of tests and of product characterisation by XRF (Table 3) were not

278 available, and thus the fact that use of MKD could result in phosphorus leaching was not known. Although

279 this affects the suitability of the product for the treatment of waters with low phosphorus concentration

280 (µg/L), it did not influence the findings obtained in this phase of the study.

281 The selected pH-adjusting products were systematically added before and after addition of solid

282 Fe2(SO4)3 and the purification results compared with those of samples treated only with solid coagulant.

283 The time of pH adjustment had a significant influence on the purification results. Addition of pH-adjusting

284 product 30 s before or after solid Fe2(SO4)3 addition had a severe negative effect on the purification

285 process, resulting in significantly higher residual concentrations of DOC and SS (Fig. 2) and of phosphorus

286 and iron (Table 5) in the treated samples. The residual charge quantity (Cq) contained in -30 and +30 s

287 samples was also substantially more negative, especially in samples where the by-products MKD and

288 MAHT were added (Fig. 2). Residual concentrations of SS and DOC in samples where pH adjustment
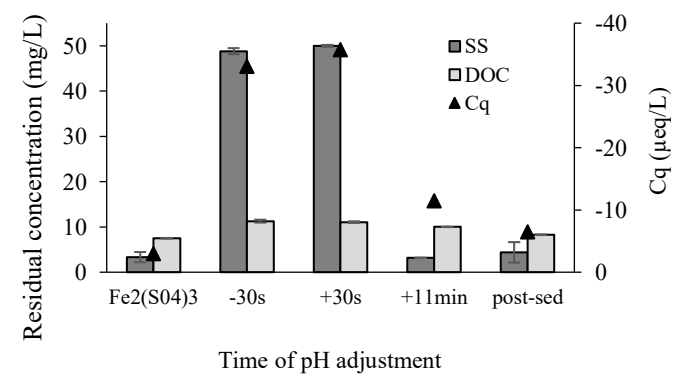
289   occurred at 11 min after solid Fe2(SO4) addition were slightly higher than those observed in samples
290   treated with solid Fe2(SO4)3 only (Fig. 2). Samples where pH adjustment occurred in the post-
291   sedimentation stage contained similar DOC and SS concentrations to samples treated with the coagulant
292   only.

293   Samples treated with MKD contained high residual phosphorus concentrations at all pH adjustment times
294   tested, but especially in the post-sediment stage of the treatment (Table 4). As expected, the adjustment of
295   pH influenced the alkalinity and acidity in the treated water. This influence was found to be dependent not
296   only on the type (carbonate, hydroxide and mixed) and dose of pH-adjusting product added, but also on
297   the time of its addition (Table 5).

a) Solid Fe2(SO4)3 80 mg/L + Ca(OH)2 8 mg/L   b) Solid $Fe_2(SO_4)_3$ 80 mg/L + Maht 40 mg/L

c) Solid $Fe_2(SO_4)_3$ 80 mg/L + MKD 40 mg/L

298

299

300   **Figure 2** – Influence of the time of pH adjustment on dissolved organic carbon (DOC), suspended solids
301   (SS) and charge quantity (Cq) in samples treated with solid $Fe_2(SO_4)_3$ (maximum and minimum values
302   of replicates indicated by error bars). Adjustment with a) analytical quality $Ca(OH)_2$, b) the by-product
303   MAHT ($Ca(OH)_2$, $CaCO_3$ and CaO) and c) the $CaCO_3$ based by-product MKD.

304

305 **Table 5** – Influence of the time of pH adjustment on the water quality of solid $Fe_2(SO_4)_3$-treated samples

306 (mean concentration ± deviation between two experiment replicates).

Sample	NH$_4$-N µg/L	Tot-P µg/L	PO$_4$-P µg/L	Alk mmol/L	Acid mmol/L	Fe mg/L	SO$_4$ mg/L	Ca mg/L	pH
Raw water	180 ±0	101 ±10	39±18	0.61 ±0.00	0.10 ±0.00	7.0 ±0.0	1.9 ±0.2	6.1 ±0.0	6.2-6.8
Fe$_2$(SO$_4$)$_3$ Solid 80 mg/L	275 ±15	9 ±1	4±1	-0.06 ±0.00	0.26 ±0.04	1.8 ±0.0	45.5 ±0.5	6.1 ±0.0	4.3
Fe$_2$(SO$_4$)$_3$+Ca(OH)$_2$ -30 s	240 ±10	56 ±7	16±2	0.08 ±0.00	0.17 ±0.02	17.5 ±0.5	44.5 ±0.5	10.2 ±0.1	5.6
Fe$_2$(SO$_4$)$_3$+Ca(OH)$_2$ +30 s	220 ±30	56 ±1	16±0	0.08 ±0.00	0.20 ±0.01	18.5 ±0.5	44.0 ±0.0	10.3 ±0.0	5.6
Fe$_2$(SO$_4$)$_3$+Ca(OH)$_2$ +11 min	275 ±5	13 ±2	7±2	0.09 ±0.00	0.12 ±0.01	2.6 ±0.5	44.0 ±0.0	10.2 ±0.0	5.7
Fe$_2$(SO$_4$)$_3$+Ca(OH)$_2$ post-sed	265 ±25	7 ±1	4±0	0.13±0.00	0.08 ±0.01	1.7 ±0.0	43.5 ±0.5	10.4 ±0.0	5.9
Fe$_2$(SO$_4$)$_3$+MAHT -30 s	215 ±45	67 ±1	45±1	0.18 ±0.02	0.15 ±0.00	18.5 ±0.5	44.0 ±0.0	12.8 ±0.4	5.9
Fe$_2$(SO$_4$)$_3$+MAHT +30 s	260 ±10	70 ±0	46±2	0.19 ±0.03	0.15 ±0.01	18.5 ±0.2	44.0 ±0.0	12.9 ±0.6	5.9
Fe$_2$(SO$_4$)$_3$+MAHT +11 min	275 ±5	9 ±2	5±1	0.19 ±0.00	0.11 ±0.01	2.2 ±0.1	44.0 ±0.0	12.7 ±0.2	6.0
Fe$_2$(SO$_4$)$_3$+MAHT post-sed	280 ±10	8 ±1	5±0	0.42 ±0.01	0.05 ±0.00	1.6 ±0.0	43.0 ±0.0	14.4 ±1.4	6.1
Fe$_2$(SO$_4$)$_3$+MKD -30 s	215 ±35	175 ±15	160±20	0.25 ±0.01	0.15 ±0.01	17.5 ±0.5	44.5 ±0.5	14.2 ±0.2	6.1
Fe$_2$(SO$_4$)$_3$+MKD +30 s	215 ±15	180 ±20	150±20	0.24 ±0.02	0.15 ±0.02	17.0 ±0.0	44.5 ±0.5	14.1 ±0.3	6.1
Fe$_2$(SO$_4$)$_3$+MKD +11 min	265 ±5	61 ±12	58±12	0.22 ±0.00	0.10 ±0.01	2.3 ±0.7	44.5 ±0.5	13.2 ±0.2	6.0
Fe$_2$(SO$_4$)$_3$+MKD post-sed	280 ±0	760 ±40	740±50	0.49 ±0.04	0.05 ±0.00	1.6 ±0.0	43.5 ±0.5	19.6 ±1.0	6.2

307 **3.2.2 Coagulation with pre-dissolved Fe$_2$(SO$_4$)$_3$**

308 The influence of pH adjustment on the purification efficiency achieved by pre-dissolved $Fe_2(SO_4)_3$ was

309 evaluated using two pH-adjusting products, the standard $Ca(OH)_2$ and the mixed base product MAHT

310 ($Ca(OH)_2$, $CaCO_3$ and CaO). The adjustment of pH before or after coagulation with pre-dissolved

311 $Fe_2(SO_4)_3$ had a measurable negative influence on purification efficiency (Fig. 3 and Table 6). However,

312 this influence was substantially less pronounced than that observed in samples treated with solid $Fe_2(SO_4)_3$

313 (Fig. 2 and Table 5). Residual DOC concentrations were slightly higher in all samples where pH

314 adjustment was performed, compared with samples treated with pre-dissolved $Fe_2(SO_4)_3$ only (Fig. 3). In

315 general, higher residual concentrations of SS, DOC, phosphorus and iron were found in samples where pH

316 adjustment occurred 30 s before coagulant addition (Fig. 3 and Table 6) compared with other pH

317 adjustment times.

a) Pre-dissolved $Fe_2(SO_4)_3$ 75 mg/L+Ca(OH)$_2$ 7 mg/L

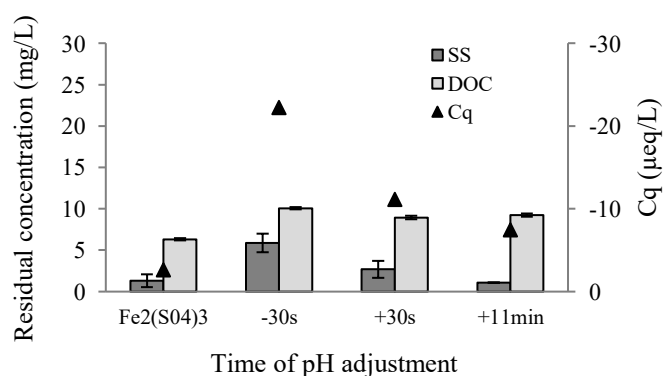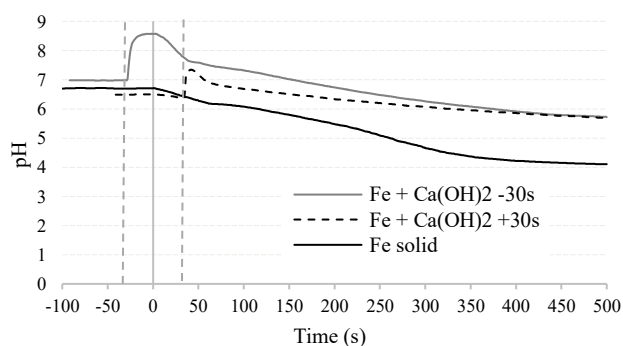b) Pre-dissolved $Fe_2(SO_4)_3$ 75 mg/L+Maht 40 mg/L

318

Figure 3 - Influence of the time of pH adjustment on dissolved organic carbon (DOC), suspended solids (SS) and charge quantity (Cq) in samples treated with pre-dissolved $Fe_2(SO_4)_3$ (maximum and minimum values of replicates represented by error bars). Adjustment with a) analytical quality $Ca(OH)_2$ and b) the by-product MAHT ($Ca(OH)_2$, $CaCO_3$ and CaO).

Table 6 - Influence of the time of pH adjustment on water quality of pre-dissolved $Fe_2(SO_4)_3$-treated samples (mean concentration ± deviation between two experiment replicates).

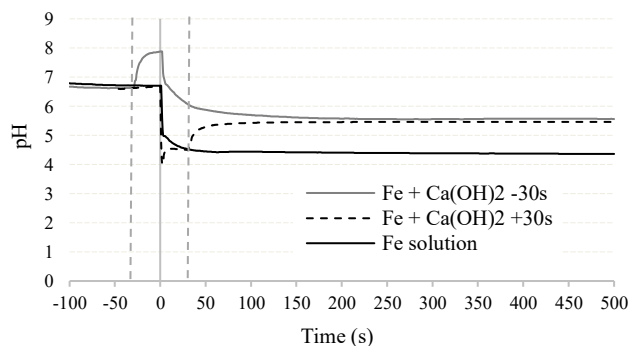| Sample	NH₄-N µg/L	Tot-P µg/L	PO₄-P µg/L	Alk mmol/L	Acid mmol/L	Fe mg/L	SO₄ mg/L	Ca mg/L	pH
Raw water	180 ±0	101 ±10	39±18	0.61 ±0.00	0.10 ±0.00	7.0 ±0.0	1.9 ±0.2	6.1 ±0.0	6.2-6.8
Fe₂(SO₄)₃ Solution 75 mg/L	270 ±20	9 ±2	5 ±1	-0.03 ±0.00	0.19 ±0.01	1.4 ±0.0	40.0 ±0.0	6.0 ±0.0	4.5
Fe₂(SO₄)₃+Ca(OH)₂ - 30 s	245 ±5	18 ±2	13 ±1	0.08 ±0.00	0.14 ±0.02	4.5 ±0.0	41.0 ±0.0	9.6 ±0.1	5.6
Fe₂(SO₄)₃+Ca(OH)₂ + 30 s	260 ±20	9 ±1	6.0 ±0	0.09 ±0.01	0.13 ±0.00	1.8 ±0.0	40.0 ±1.0	9.6 ±0.1	5.6
Fe₂(SO₄)₃+Ca(OH)₂ + 11 min	285 ±5	7 ±1	5.0 ±1	0.07 ±0.01	0.12 ±0.01	1.3 ±0.0	40.5 ±0.5	9.4 ±0.1	5.6
Fe₂(SO₄)₃+MAHT - 30 s	235 ±25	22 ±1	14 ±1	0.19 ±0.04	0.12 ±0.01	5.7 ±0.0	39.5 ±0.5	11.6 ±0.8	5.9
Fe₂(SO₄)₃+MAHT + 30 s	250 ±0	10 ±0	7 ±0	0.18 ±0.00	0.11 ±0.00	1.7 ±0.0	39.0 ±0.0	11.5 ±0.0	6.1
Fe₂(SO₄)₃+MAHT + 11 min	245 ±25	8 ±0	6 ±1	0.21 ±0.00	0.11 ±0.00	1.1 ±0.0	40.0 ±1.0	12.4 ±0.6	6.1

4. Discussion

The difference in the required dose for effective coagulation between pre-dissolved and solid $Fe_2(SO_4)_3$ indicates that pre-dissolution of the coagulant had a measurable influence on the coagulation and flocculation processes. The SUVA value of the runoff water (3.27 L/mg-m) indicates its humic nature (Matilainen et al., 2010). In the chemical treatment of acidic and humic waters by metal salt addition, charge neutralisation/precipitation is believed to be the dominant coagulation mechanism (Duan and Gregory, 2003; Wei et al., 2009; Matilainen et al., 2010). In the present study, this was supported by the effect of increasing doses of coagulant on surface charge or charge quantity (Cq) in solution and the near zero charge found in samples where optimum removal of colour and turbidity was achieved (Fig. 1c). Variations in the pH of water samples treated with solid and pre-dissolved $Fe_2(SO_4)_3$ in which pH adjustment was conducted 30 s before and after coagulant addition are presented (Fig. 4). It is reasonable to conclude that the higher dosage required for solid $Fe_2(SO_4)_3$ compared with pre-dissolved $Fe_2(SO_4)_3$ is linked to the slow dissolution of the solid coagulant (vestiges of the solid coagulant could be seen up to 5 min after dosing). Portions of the solid coagulant went through hydrolysis reactions at different times, so as the dissolution progressed these reactions occurred under different conditions (e.g. in terms of pH, DOC concentration etc.). This might have resulted in e.g. formation of metal hydroxide species with lower charge neutralisation capacity, as well as less formation of metal hydroxide precipitates. This would explain the additional dosage of solid coagulant required to enable charge neutralisation to occur and for effective coagulation and flocculation to be achieved.

344   All pH-adjusting products tested were capable of increasing the pH of the water to values between 5.5 and

345   6.5 (Table 4) at somewhat reasonable doses. The observed differences in required dose can be linked to

346   the purity and chemical composition of individual products. By-products required higher doses than

347   commercially available materials and $CaCO_3$-based products required higher doses than products

348   containing $Ca(OH)_2$ and CaO (Table 4). The neutralisation mechanisms of different products are

349   exemplified in the pH response curves obtained (Fig. 4). Addition of $Ca(OH)_2$ and the by-product MAHT

350   ($Ca(OH)_2$, $CaCO_3$ and CaO) resulted in a fast increase in pH due to the fast reactions of $Ca(OH)_2$ and CaO,

351   while addition of the by-product MKD resulted in a gradual increase in pH values due to slower reactions
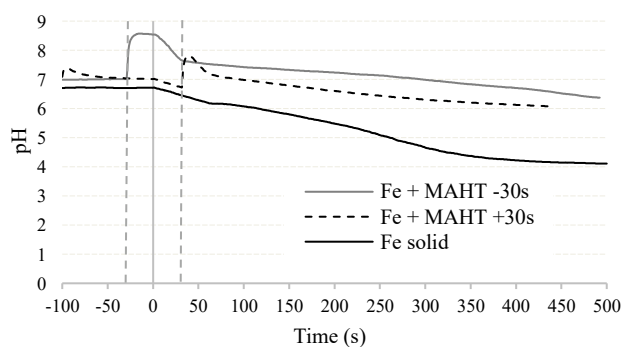
352   involving $CaCO_3$.
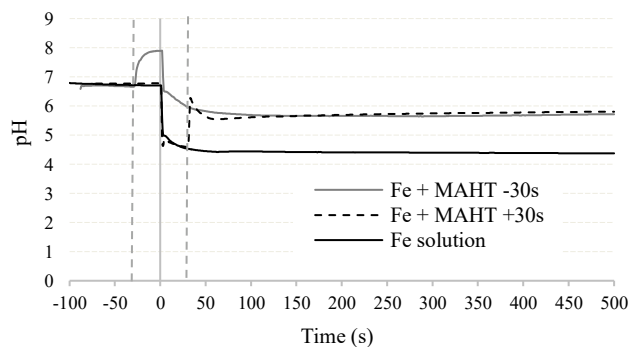
a) $Fe_2(SO_4)_3$ solid 80 mg/L + $Ca(OH)_2$ 8 mg/L

b) $Fe_2(SO_4)_3$ solution 75 mg/L + $Ca(OH)_2$ 8 mg/L

353

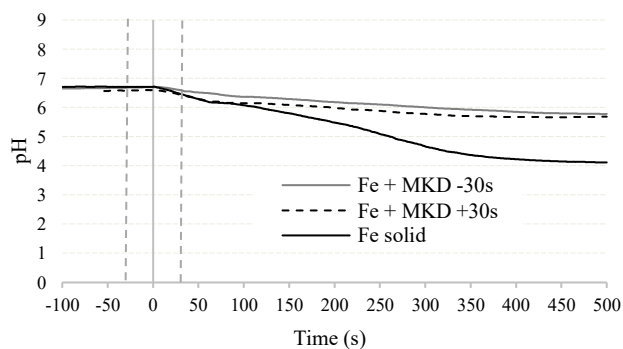c) $Fe_2(SO_4)_3$ solid 80 mg/L + MAHT 40 mg/L

d) $Fe_2(SO_4)_3$ solution 75 mg/L + MAHT 40 mg/L

354

e) $Fe_2(SO_4)_3$ solid 80 mg/L + MKD 40 mg/L
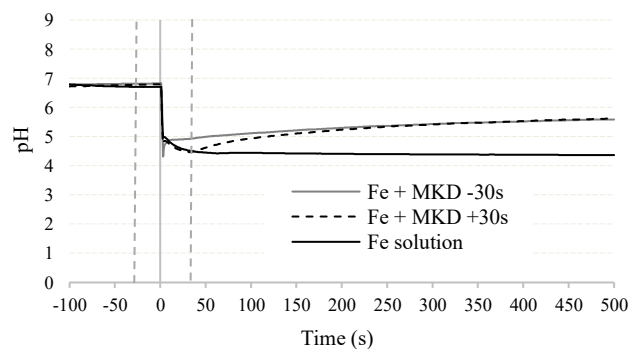
f) $Fe_2(SO_4)_3$ solution 75 mg/L + MKD 40 mg/L

355

356 **Figure 4** – Variation in pH in the solution over time due to addition of solid $Fe_2(SO_4)_3$ (a, c, e) and pre-
357 dissolved $Fe_2(SO_4)_3$ (b, d, f) and pH adjustment with analytical quality $Ca(OH)_2$ (a, b), the by-product
358 MAHT (c, d) and the by-product MKD (e, f) 30 s before or after addition of the coagulant..

359 The time of pH adjustment in relation to time of coagulant addition had a significant influence on
360 purification results, especially when solid $Fe_2(SO_4)_3$ was applied. The pH at which coagulation takes place
361 is known to have a significant effect on the coagulation mechanisms that occur (Duan and Gregory, 2003;
362 Cheng, 2002; Jiang and Wang, 2009; Slavik et al., 2012). Increasing pH levels result in the ionisation of
363 carboxylic and phenolic functional groups of humic acids, leading to a net increase in DOC negative
364 surface charges. Furthermore, at higher pH the hydrolysis species of metal salt coagulants formed are of a
365 monomeric and less positive nature, so as a result the required dose for effective coagulation increases
366 with increasing pH (Cheng, 2002; Jiang and Wang, 2009). The coagulant dose required for samples where
367 pH adjustment was performed prior to addition of the coagulant was not evaluated, as the aim of the study
368 was to investigate the effect of pH adjustment at constant coagulant dosage. Therefore, lower purification
369 efficiency was to some extent expected for samples where pH adjustment occurred prior to coagulant
370 addition. This could be seen during experiments where pre-dissolved coagulant was applied (Fig. 3).
371 Higher SS and DOC residual concentrations were found in samples where pH adjustment was conducted
372 30 s prior to coagulant addition. Furthermore, no benefits of adding $Ca(OH)_2$ prior to addition of the
373 coagulant, as an aid in floc formation, were observed during our experiments. The influence of pH
374 adjustment 30 s prior to or after coagulant addition was significantly more accentuated than expected for
375 the performance of solid $Fe_2(SO_4)_3$ (Fig. 2). It is clear that the addition of pH-adjusting products had a
376 significant effect on dissolution of the coagulant and mostly halted the coagulation process. In coagulation
377 of humic water, acidic pH levels result in higher removal of DOC at lower coagulant doses. Therefore, pH
378 adjustment prior to coagulant addition is not recommended. When pre-dissolved or liquid coagulants are
379 used the coagulation process is very fast, and thus pH adjustment soon after coagulant dosing can be
380 accomplished.

381 Purification results obtained when pH adjustment was conducted during the flocculation stage of the
382 treatment processes were very similar. Neutralisation of pH during the flocculation stage was carried out
383 in the third phase of tests (overall purification efficiency was evaluated) and the fourth phase of tests
384 (influence of the time of pH adjustment was evaluated). Slightly higher residual DOC concentrations were
385 found in samples where pH adjustment took place at 15 min (Table 4) or 11 min (Fig. 2 and Fig. 3) inside
386 the purification process for both solid and pre-dissolved coagulants. Hence, since coagulation had already
387 occurred when pH adjustment was performed, it can be assumed that the increase in pH caused
388 solubilisation of metal-humic complexes resulting in an overall higher DOC concentration in treated

389 samples. This was also reported by Slavik et al. (2012), who investigated the influence of changes in water

390 pH on DOC removal during the coagulation and flocculation processes. The adjustment of pH during the

391 flocculation stage appears not to have influenced the properties and settling characteristics of flocs formed.

392 In line with findings by Gregor et al. (1997), similar SS concentrations were found in all treated samples

393 at the end of the sedimentation period, despite the addition of pH-adjusting products mid-way through the

394 flocculation process (Table 4, Fig. 2 and Fig. 3). For samples where pH adjustment was performed after

395 the sedimentation stage (post-sed), the quality of purified water was similar to that obtained in samples

396 treated only with solid $Fe_2(SO_4)_3$. Slightly higher SS concentration was found in samples where pH

397 neutralisation was conducted, with the highest values found in samples where the by-products MAHT and

398 MKD were added (Fig. 2).

399 Regarding the overall performance and suitability of the products tested, the paper industry by-product

400 Pmud cannot be recommended. It required higher doses and its application resulted in low purification

401 efficiency, with high SS, TSS and DOC residual concentrations in the treated samples. The lime industry

402 by-products, LKD and MKD, appear to contain substantial amounts of non-reactive substances, leading to

403 high TSS concentration in treated samples. Higher sediment production results in an increased need for

404 sedimentation basin maintenance and cleaning and a larger sediment/sludge storage area, increasing the

405 costs of treatment. Furthermore, leaching of phosphorus occurred when MKD was applied. Therefore,

406 LKD and MKD can also be considered unsuitable for the use evaluated here. They might represent a viable

407 option for SS- and phosphorus-rich waters subjected to chemical treatment. The product FC7 showed good

408 performance and can be a suitable option for systems where CaCO3-based products are applicable. The

409 by-products of the paper industry (MAHT) and cement industry (CKD) performed well and can be

410 considered viable options for adjustment of pH in chemically treated runoff waters. Their cost-

411 effectiveness will depend mainly on transport costs and should be evaluated on a case-by-case basis.

5. Conclusions

413 A lower dose (5-10%) of pre-dissolved $Fe_2(SO_4)_3$ was required for effective coagulation of the humic water

414 tested compared with solid $Fe_2(SO_4)_3$. All calcium-based products tested proved capable of increasing the

415 pH of chemically treated runoff water from around 4 to ≥ 5.5 inside the retention time allowed (<60 min)

416 and in moderate doses. The time of pH adjustment relative to time of coagulant addition had a significant

417 influence on the purification results, especially when solid $Fe_2(SO_4)_3$ was used. Overall, higher residual

418 concentrations of DOC and TSS were found in all samples where pH adjustment occurred. Furthermore,

419 no benefits of adding $Ca(OH)_2$ prior to addition of the coagulant, as an aid in floc formation, were observed

420 in experiments. The increase in pollutant concentration depended on the type of pH-adjusting product and

421   time of its application, but especially on the type of coagulant (solid or pre-dissolved) used. Adjustment

422   of pH just before or after solid coagulant addition appeared to affect its dissolution and the reactions which

423   followed, and had a significant negative influence on the purification process. Lower coagulant doses and

424   higher removal of DOC were achieved in treatment of humic water samples at acidic pH levels. Therefore,

425   pH adjustment prior to coagulant addition is not recommended. When pre-dissolved or liquid coagulants

426   are used the coagulation process is very fast, and thus pH adjustment soon after coagulant addition is

427   possible. According to the results obtained, pH adjustment should be carried out during the flocculation

428   stage of the chemical purification process or at the outlet of the sedimentation basin. This is especially

429   recommended if solid coagulants are applied. Regarding the performance of the pH-adjusting products

430   tested, based on required dose and overall influence on purification efficiency, the paper industry by-

431   product MAHT and the cement industry by-product CKD performed well and can be considered viable

432   options for adjustment of pH in chemically treated waters.

Acknowledgements

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