

Use of the BCR sequential extraction procedure for element fractionation in activated sludge from the pulp and paper mill

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In this study, the elements in the activated sludge were fractionated between acid-soluble (CH_3COOH ; BCR1), reducible ($\text{NH}_2\text{OH}\cdot\text{HCl}$; BCR2) and oxidisable ($\text{H}_2\text{O}_2 + \text{CH}_3\text{COONH}_4$; BCR3) fractions. Only the extractable concentrations of Mn (523 mg kg^{-1} ; d. w.), Ni (5.1 mg kg^{-1} ; d. w.), S (1650 mg kg^{-1} ; d. w.) and Ti (1.3 mg kg^{-1} ; d. w.) in the BCR1 fraction were higher than those in the BCR2 fraction. The extractable concentration of Mn in the BCR1 fraction was also higher than that (160 mg kg^{-1} ; d. w.) in the BCR2 fraction and that (135 mg kg^{-1} ; d. w.) in the BCR3 fraction. However, if we disregard elements whose concentrations were lower than the detection limits, as well as Ba and Mn, the extractable concentrations of other element in the BCR3 fraction were higher than those in the BCR1 and BCR2 fractions. The recovery values (R% values), which are the ratio of sum of BCR sequential extraction procedure to the total digestion using USEPA method 3051A, varied between 81.6% (Ni) and 96.4% (V). Due to the high R% values for certain elements we would like to point out that caution must always be exercised when activated sludge is utilized and the existing legislation must always be applied.

Key words: BCR, extraction, pulp and paper mill, wastewater sludge, waste

INTRODUCTION

Water is the driving force for pulp and paper mills. Each pulping process utilizes large amounts of water, which reappear in the form of effluent. Closing the water circles and achieving an overall reduction in water consumption have been among the most important aims in the pulp and paper mill industry for many years. When water is recirculated within the mill, all of the impurities in the water are concentrated and they

have to be removed as solid wastes or stripped into air in gaseous form [1]. Depending on the treatment to which the effluents from the pulp and paper process industry have been subjected, the wastewater, before discharged into the receiving water bodies, usually undergoes primary and secondary treatment at the activated sludge plant. This results in considerable amounts of wastewater sludge, which is called an activated sludge.

An activated sludge originated from a wastewater treatment plant is one of the largest by-products of the pulp and paper industry and is usually disposed of in landfills or

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incinerated. However, the rise in the costs of landfill, as a waste management option, driven by regulations designed to protect human health and the environment, has led to problems in acquiring new sites for disposal purposes. Therefore, solid waste generation represents a continuing disposal problem for the forest industry. In addition, utilization aspects and environmental management systems are the driving forces in minimizing the formation and disposal of solid wastes in the pulp and paper industry. The utilization of solid wastes allows industry to reduce its reliance on the landfill option, reuse and recycle residues or even utilize materials as beneficial products in line with the objectives of European Union laws [2]. There is therefore a growing trend towards seeking options for the utilization of solid wastes in the Finnish pulp and paper industry. On the basis of the above mentioned facts, during the past decade in the Finnish forest industry there has been a movement towards a common strategy for all forms of waste, with the priority set on reusing waste materials and, if possible, taking advantage of their materials or energy content. Utilization of solid waste allows industry to implement the 3R principle, reduce, reuse and recycle [3].

Heavy metals occur in wastewater treatment sludge in various physicochemical forms, such as soluble, adsorbed, exchangeable, precipitated, organically complexed and residual phases. Heavy metals may also occur in biological forms, such as species in the extracellular and intracellular spaces of plant tissue. Natural and anthropogenic environmental changes greatly influence the behaviour of metallic pollutants in sludge, as the form in which they occur can be changed. Such external factors can include pH, temperature, the redox potential, organic matter decomposition, leaching, ion exchange processes and microbiological activity [4]. Therefore, it is necessary to know the physical and chemical properties of sludges before their disposal, and particularly their elemental contents, both in terms of total concentrations and the amount that is potentially biologically effective [5]. Extraction (leaching) procedures are widely used for the assessment of heavy metal mobilization. Extraction procedures are undertaken to evaluate the metal availability and bioavailability. To study trace metal partitioning in industrial wastes, different schemes have been proposed based on application of sequential procedures, yielding the so-called operational speciation. Many of these are variants on the extraction scheme proposed by Tessier et al. [6]. As part of an attempt to harmonize methodology for the extraction/leaching test throughout the European Community, the European Community Bureau of Reference (BCR), now the Standards, Measurement and Testing Program, developed a three-stage, sequential extraction protocol, in which metals are divided into acid soluble/exchangeable, reducible and oxidisable fractions [7].

The objective of this work was to study the main important physical and chemical properties, as well as the total and extractable heavy metal concentrations of heavy metals in the activated sludge originating from the biological wastewater

treatment plant of a Finnish pulp and paper mill complex. In Finland, and elsewhere in the European Union (EU), the properties of solid wastes, especially when they are utilized or taken to a landfill, have to be investigated. The general principle applied in utilization and in landfill approval is that the composition and extractability of waste have to be known. Sequential extraction studies are often applied in assessing worst-case environmental scenarios, in which the individual component of the sample becomes soluble and mobile [8–9].

MATERIALS AND METHODS

Wastewater treatment at the mill – activated sludge sampling procedure

The activated sludge investigated in this study is a combination of sludge from the primary and secondary clarifiers at the biological wastewater treatment plant at an integrated pulp and paper mill complex located in Finland [10]. The “integrated pulp and paper mill complex” combines a pulp mill and a paper mill located on the same site [11]. The “sludge” is a general term for the residue that results from the pulp and papermaking. Sludge is produced at two steps in the process of treating the effluent. Primary sludge is recovered by the first stage of the process at the primary clarifier. Primary clarification is usually carried out by sedimentation, but can also be performed by dissolved air flotation. Secondary treatment is usually a biological process in which micro-organisms convert the waste to carbon dioxide and water while consuming oxygen. The resulting solids are then removed through clarification in the secondary treatment.

The mill investigated in this study produced elemental chlorine-free (ECF) bleached soft and hardwood pulp (339 850 t), uncoated fine paper (481 810 t), coated printing papers (364 040 t), and sawn goods (152 900 t) in 2011, and for this, consumed 48 m³ process water/t of pulp and 8 m³ process waste/t of paper produced. The activated sludge wastewater treatment plant, i. e. a biological wastewater treatment plant, has two aeration basins in series with a total volume of 87 000 m³. The designed wastewater discharge is 60 000 m³/d. The hydraulic retention is 35 hours in the aeration stage and 48 hours in the wastewater treatment plant [12–13]. Approximately one third of the activated sludge investigated in this study is from the primary clarifier and two thirds from the secondary clarifier. In the forest industry, these sludges are typically purged from the process into the same mixing tank in order to minimize handling and transport costs at the mill. Mixing of these sludges is also necessary because the primary sludge increases the dry matter content of the mixture after dewatering. Sampling was carried out over a period of three days, where individual daily samples of one kg were combined to give one composite sample with a weight of 3 kg (wet weight). The sampling period represented normal process operating conditions for the pulp and paper mill. After sampling, the samples were stored in polyethylene bottles in a refrigerator

(+4 °C) because the sample was not impossible to analyse immediately. The sample should be analysed as soon as possible after sampling. However, if this is not done, according to EPA [14], the sample should be chemically/physically preserved as soon as possible after sampling in order to avoid/minimise biological, chemical or physical changes that can occur between time of collection and analysis. For the above-mentioned reason, we decided to follow the procedure of Sarode et al. [15] and to store the sample in a refrigerator until analysis. A coning and quartering method was applied repeatedly to reduce the sludge sample to a size suitable for conducting laboratory analyses [16].

Determination of the mineral composition, physical and chemical properties of sludge

For the determination of the mineralogical composition of the sludge, an X-ray diffractogram was obtained with a Siemens D 5000 diffractometer (Siemens AG, Karlsruhe, Germany) using CuK α radiation. The scan was run from 2 to 70° (2-theta-scale), with increments of 0.02° and a counting time of 1.5 seconds per step. Operating conditions were 40 kV and 40 mA. Peak identification was carried out with a DIFFRAC-plus BASIC Evaluation Package PDFMaint 12 (Bruker AXS, Germany) and ICDD PDF-2 Release 2006 software package (Pennsylvania, USA).

Determination of pH and the electrical conductivity (EC) in the sludge was carried out according to the European Standard SFS-EN 13037 at a solid to liquid (i. e. ultrapure water) ratio of 1 : 5. Determination of the dry matter content (DMC) of the sludge was carried out according to the European Standard SFS-EN 12880, in which a sample is dried overnight to a constant mass in an oven at 105 °C. The organic matter content, as measured by the loss-on-ignition (LOI), was determined according to the European Standard SFS-EN 12879, in which an oven-dried (105 °C) sample is heated overnight in a muffle furnace (Box Furnace, Lindberg, Blue M, Asheville, USA) at the temperature of 550 °C. The total organic carbon (TOC) content was determined according to the European Standard SFS-EN 13137 using a Leco CHN-600 analyser (Leco Inc., USA), in which a sample is combusted and the evolved carbon dioxide is measured by infrared spectrometry. The neutralizing (liming effect) value (NV) and reactivity value (RV) were determined according to the European Standards SFS-EN 12945 and SFS-EN 13971, respectively. A comprehensive review of the standards, analytical methods and instrumentation is given in our previous study [17].

Determination of the total nitrogen concentration in the sludge was carried out according to the European Standard SFS-EN 13654-1 by the Kjeldahl method using a Foss-Tecator Kjeltec 2300 Analyzer (Höganäs, Sweden) equipped with a Foss-Tecator 2020 Digester (Höganäs, Sweden). The determination of easily soluble plant nutrient (Ca, Mg, Na, K, P, S, Cu, Zn and Mn) concentrations in the sludge was carried out according to the procedure of MTT Agrifood Research Finland, in which the easily soluble forms of Ca, Mg, Na, K,

P, S, Cu, Zn and Mn were extracted with 0.5 M acidic ammonium acetate (pH 4.65). However, in the extraction of Cu, Zn and Mn, the acidic (pH 4.65) ammonium acetate extract contained 0.02 M ethylenediaminetetra-acetic acid disodium salt (Na₂EDTA). In both extraction procedures, one volume part of a dry sample was shaken with ten parts of extraction solution for 1 h. Before analysis, the extract was separated from the solid residue by filtration through a 12.5 mm diameter Schleicher & Schull 589 blue ribbon filter paper (Schleicher & Schull, Dassel, Germany). The concentrations of Ca, Mg, Na, K and S were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo Elemental Iris Intrepid II XDL, Franklin, USA), and the concentrations of Cu, Zn and Mn by a flame atomic absorption spectrometer (FAAS, Perkin Elmer Analyst 700, Norwalk, USA). The concentration of P in the extract was determined spectrophotometrically by the molybdenum blue method using an automatic Foss-Tecator FIASStar 500 Flow Injection Analyser (Högnés, Sweden). Before the nutrient determination on the sludge, the sample was dried overnight to constant mass at 105 °C in a drying oven (Termaks) according to the European Standard SFS-EN 12880. A comprehensive review of the standards, analytical methods and instrumentation is given in our previous study [17].

Determination of total element concentrations in the sludge

For the determination of total element concentrations in the sludge, a dried sample was digested with a mixture of HCl (3 mL) and HNO₃ (9 mL) in a CEM Mars 5 microprocessor controlled microwave oven with CEM HP 500 Teflon vessels (CEM Corp., Matthews, USA) using the USEPA method 3051A [18]. The cooled solution was transferred to a 100 mL volumetric flask and the solution was diluted to volume with ultrapure water. All reagents and acids were suprapure or pro analysis quality. Except for Hg, the total element concentrations in the sludge were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES). The concentration of Hg in the sludge was determined with a Perkin Elmer Analyst 700 cold-vapour atomic absorption spectrometer (Norwalk, USA). The comprehensive review of the analytical methods and instrumentation is given in our previous study [17].

Sequential extraction of elements in the sludge

For the fractionation of elements in the activated sludge between the exchangeable (CH₃COOH), easily reduced (NH₂OH-HCl in nitric acid medium) and oxidisable (H₂O₂ + CH₃COONH₄) fractions, we used the three-stage sequential extraction procedure, which is illustrated in our previous publication [17]. This extraction procedure is widely used for the fractionation of heavy metals in various environmental materials, e. g. industrial sludge [4, 9]. The procedure was developed by the European Standards, Measurement and Testing (SM&T) Programme, formerly the European Community

Bureau of Reference (BCR). Therefore, in this manuscript, we have used the abbreviations “BCR1” for the exchangeable fraction, “BCR2” for the easily reduced fraction and “BCR3” for the oxidisable fraction.

The sequential extraction was carried out by shaking 1 g of the sludge in a polypropylene bottle. In order to minimize possible chemical and/or microbiological changes in the material, the extraction was carried out using the sample as such, instead of a dried sample, since according to Kosson et al. [19], it is preferable to avoid sample drying before extraction. After each extraction step, the extracts were separated from the solid residue by filtration through a 0.45 µm membrane filter (47 mm diameter; Schleicher & Schuell, Dassel, Germany). In order to avoid losses between the extraction stages, the filters and adhering sludge particles from the previous extraction stage were also included in the next stage. After the addition of 200 µL of 65% HNO₃ to the supernatant phase, it was stored in a refrigerator (+4 °C) until element determinations [14–15]. The element concentrations in the extracts (i. e. extraction stages 1–3) were determined with a Thermo Fisher Scientific iCAP6500 Duo (United Kingdom) inductively coupled plasma optical emission spectrometer (ICP-OES).

RESULTS AND DISCUSSION

Mineral composition, physical and chemical properties of the sludge

The most important physical and chemical properties of the sludge are given in Table 1. Although XRD analysis can be useful in identifying the chemical species of crystalline particles, in our case only calcite (CaCO₃; 87.3%) and quartz (SiO₂; 12.7%) could be identified (Figure). The pH of the

sludge was neutral (pH 6.9). This is reasonable in the light of the fact that the pH value in the activated sludge plant of the mill investigated in this study is typical between 7 and 8 which pH value is required for the optimal action of microbes living in the activated treatment plant. The pH of our sludge agrees with the findings of Suriyanarayanan [20], who reported pH value of between 6.7 and 7.0 for activated sludge. According to the electrical conductivity value (1.4 mS cm⁻¹), which is an index of the total dissolved electrolyte concentrations, the leaching solution of the sludge investigated in this study has a very low ionic strength.

The very high total organic carbon (TOC) value of 405 g kg⁻¹ (d. w.) and the loss-on-ignition (LOI) value of 71.8% (d. w.) indicate that the organic matter content in the sludge is high. The high values of these parameters are reasonable in the light of the fact that the main organic components of the sludge are biomass originated from the process raw materials, i. e. wood and bark residues, cellulose fibres, hemicellulose, and lignin. To some extent, it also contains organic binders and process chemicals which enter the activated sludge wastewater treatment plant via the process water flows circulating in the processes. In this context it is worth noting that although loss-on-ignition (LOI) is a common and widely used method to estimate the organic matter content of waste materials, according to Heiri et al. [21], reactions other than the burning of organic matter, e. g. dehydration of clay minerals or metal oxides, the loss of volatile compounds, or loss of inorganic carbon (i. e. CO₂) in minerals, can take place during the determination of LOI at 550 °C. Thus, LOI is an indirect measure of the organic matter content of the sludge. The dry matter content of the activated sludge was only 20.6%, which means that incineration of this residue is uneconomic due to energy requirement for driving off mois-

Table 1. Physical and chemical properties of the activated sludge and the nutrient concentrations in local mineral soil located in the Ostrobothnia region in the province of Oulu, Finland [25]

Parameter	Unit	Sludge	Coarse mineral soil
pH (1 : 5)		6.9	
Electrical conductivity (EC)	mS cm ⁻¹	1.4	
Loss-on-ignition (LOI; 550 °C)	% (d. w.)	71.8	
Total organic carbon (TOC)	g kg ⁻¹ (d. w.)	405	
Dry matter content (105 °C)	%	20.6	
Neutralizing value (NV)	% (Ca; d. w.)	10.1	
Reactivity value (RV)	% (Ca; d. w.)	10.0	
RV/NV	%	99.0	
Total N	mg kg ⁻¹ (d. w.)	16 500	
P (NH ₄ Ac)	mg kg ⁻¹ (d. w.)	270	11.7
Ca (NH ₄ Ac)	mg kg ⁻¹ (d. w.)	87 500	960
Na (NH ₄ Ac)	mg kg ⁻¹ (d. w.)	5 500	14
K (NH ₄ Ac)	mg kg ⁻¹ (d. w.)	1 000	77
Mg (NH ₄ Ac)	mg kg ⁻¹ (d. w.)	1 900	135
S (NH ₄ Ac)	mg kg ⁻¹ (d. w.)	1 600	23
Mn (NH ₄ Ac + Na ₂ EDTA)	mg kg ⁻¹ (d. w.)	790	28
Cu (NH ₄ Ac + Na ₂ EDTA)	mg kg ⁻¹ (d. w.)	6.4	3.3
Zn (NH ₄ Ac + Na ₂ EDTA)	mg kg ⁻¹ (d. w.)	160	3.8

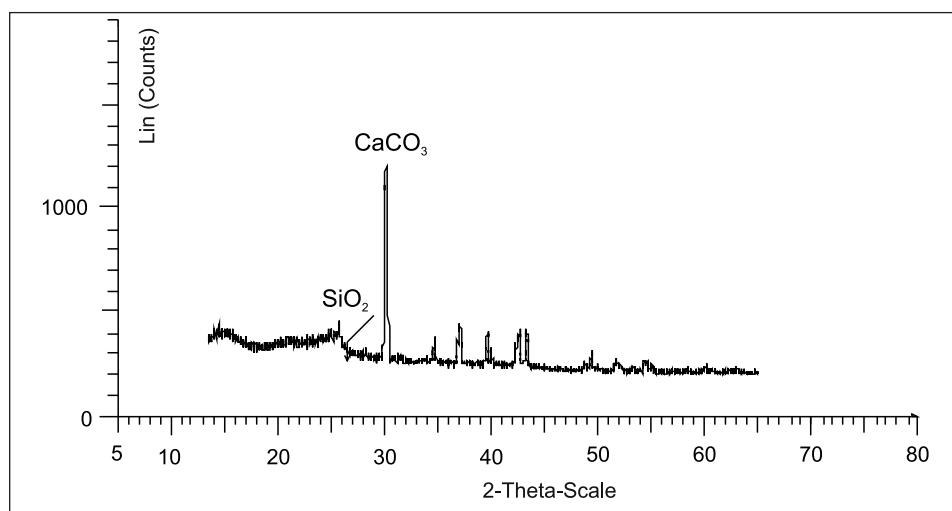


Figure. XRD data of the activated sludge

ture. However, although the incineration of activated sludge does not create any net energy, it is commonly incinerated in the power plants of the pulp and paper mills in order to avoid the handling and landfill disposal costs for this residue. From an environmental and utilization point of view, the high organic matter content in the activated sludge indicates that composting, land application and soil improvement are also attractive potential alternatives to incineration or final disposal via landfill. According to Cabral et al. [22] and Gascó et al. [23], a high organic matter content in sludge is reported to have favourable effects on the physical, chemical and microbiological properties of soil, including improvement of soil structure as well as water infiltration rate, reduce soil crusting and run-off, and improve pore-size distribution and aggregate stability to raindrop impact, as well as improving the water holding capacity of soil.

The neutralizing value (NV) of 10.1% expressed as Ca equivalent (d. w.) indicates that 3.76 tonnes of the activated sludge investigated in this study would be required to replace 1 tonne of a commercial ground limestone produced by SMA Mineral Ltd., the neutralizing value of which is 38% (Ca equivalents; d. w.). The reactivity value (RV) was determined in order to access the speed and effectiveness of the neutralizing potential of sludge as a liming material. The RV/NV ratio (%) indicates that the "fast acting" capacity is ca. 99.0% for sludge meaning that the activated sludge has an excellent liming effect and is therefore a potential soil conditioner and a pH buffer. According to literature [20, 24], the landspreading of activated sludge from pulp and paper mills has successfully been applied, for example, to forest soil to increase soil organic matter, improve soil physical properties, and to increase soil pH.

Total nitrogen and easily soluble plant nutrient concentrations in the sludge

The concentrations of total nitrogen and easily soluble plant nutrients in the studied activated sludge are given in Table 1.

The easily soluble nutrient concentrations were ca. 1.9 (Cu) and 392 (Na) times higher in the sludge than the typical values of 3.3 mg kg⁻¹ (d. w.) for Cu and 14 mg kg⁻¹ (d. w.) for Na, found in coarse mineral soils located in the Ostrobothnia region in the province of Oulu, Finland [25]. The high total nitrogen (16 500 mg kg⁻¹; d. w.) and high easily soluble forms of calcium (87 500 mg kg⁻¹; d. w.), sodium (5 500 mg kg⁻¹; d. w.), potassium (1 000 mg kg⁻¹; d. w.), magnesium (1 900 mg kg⁻¹; d. w.), manganese (790 mg kg⁻¹; d. w.) and zinc (160 mg kg⁻¹; d. w.) concentrations indicate that the activated sludge is a potential agent for soil reclamation and improving soil fertility. The elevated Ca, Mg, Na and S (1 600 mg kg⁻¹; d. w.) concentrations in the sludge are reasonable since calcium is the most abundant mineral nutrient in wood [23] and magnesium sulphate is used during the oxygen delignification process and sodium in the form of Na₂S, NaOH and Na₂SO₄ is used as cooking chemical in the pulp mill investigated in this study. The elevated calcium concentration in the sludge is also reasonable due to the fact that, at the investigated pulp and paper mill complex, their green liquor dregs are utilized as a neutralizing agent for acidic wastewaters [10, 26]. When used for neutralizing purposes for acidic wastewaters, green liquor dregs, which have a high calcium concentration of approximately 85 000 mg kg⁻¹ (d. w.), are mixed with water in a tank and fed into the acidic wastewaters prior to the activated sludge plant. The total nitrogen concentration of 16 500 mg kg⁻¹ (d. w.) (=1.65%; d. w.) in our activated sludge are consistent with the finding of Rashid et al. [27], who reported that combined sludge usually contains between 1.0 and 2.5% of nitrogen by dry weight. In addition, our nitrogen concentration in the activated sludge agrees with the value of 1.6% (d. w.) reported by Lohiniva et al. [28] for Finnish pulp and paper mills. However, it is worth noting that nutrient concentrations in sludge vary according to the pulping and papermaking process used, and the level of microbial decomposition that has occurred during secondary treatment. Furthermore, the nutrient concentrations in sludge vary widely

Table 2. Total and extractable concentrations of elements (mg kg^{-1} ; d. w.) in the investigated sludge, as well as total concentration of elements (mg kg^{-1} ; d. w.) in sludge from Finnish pulp and paper mills [28] and the recovery R (%) values of the extraction procedure [43]

Element	Total concentration of elements in the investigated sludge	Total concentration of elements in sludge from Finnish pulp and paper mills	Extractable concentrations of elements in the fractions of investigated sludge				
			BCR1	BCR2	BCR3	$\Sigma 1-3$	R, %
Al	2960		13.9	80.9	2 680	2 774.8	93.7
As	<3	1.5	<0.6	<0.6	<0.8	<2.0	
Ba	210	332	57.9	63.1	63.1	184.1	87.6
Cd	2.51.1	0.6–0.9	<0.08	0.1	2.3	<2.48	
Co	<1.0	1.9	<0.2	<0.2	0.6	<1.0	
Cr	19	16–22	<0.4	<0.4	12.8	<13.6	
Cu	33	25–43	<0.4	<0.4	32.0	<32.8	
Be	<1.0		<0.2	<0.2	<0.3	<0.7	
Fe	2620		6.7	321	2 110	2 437.7	93.0
Mn	880	1 660	523	160	135	818	92.9
Sb	<3.0		<0.6	<0.6	<0.8	<2.0	
P	3 090		182	441	2 270	2 893	93.6
Mo	1.5		<0.2	<0.2	1.0	<1.4	
Ni	19	6–11	5.1	1.4	9.0	15.5	81.6
Pb	5.2	0.3–4.3	<0.6	<0.6	4.4	<5.6	
S	9 680		1 650	409	6 660	8 719	90.1
V	28	24.5	1.1	3.1	22.8	27.0	96.4
Zn	290	193	55.2	66.7	150	271.9	93.7
Se	<3.0		<0.8	<0.8	<1.0	2.6	
Ti	<50		1.3	<0.8	34	36.1	

depending on the type of pulp and paper being produced, and the type of raw material used. The easily soluble nutrient concentrations (see Table 1) are generally lower than the total ones for Cu, Mn, P, S and Zn (see Table 2), due to the fact that ammonium acetate extraction gives only the nutrients in easily soluble form, and is therefore widely used as an indicator of plant nutrient availability [29].

Total element concentrations in the sludge

The total element concentrations in the studied activated sludge, and the literature values of elements in activated sludge originated from Finnish pulp and paper mills [28], as well as the variation of element concentrations in a Finnish non-contaminated soil [30], are presented in Table 2. The low values for heavy metals in sludge become apparent if this comparison is made. In addition, the very high easily soluble calcium concentration of $87\,500\text{ mg kg}^{-1}$ (d. w.) supports the utilization of this residue, for example, as a soil amendment agent material since according to Rato Nunes et al. [31], one measure of suitability of organic residues as a nutrient source for plant growth is the ratio of the contents of Ca to Mg. It is generally accepted that this ratio should be a minimum of 6 : 1. The sludge investigated in this study has a Ca/Mg ratio of 46 : 1, indicating that no adjustment by liming is needed. Therefore, both the very low metal and elevated calcium concentrations support the beneficial utilization of this residue in soil amendment instead of its final disposal to landfill, since it would be both economically and ecologically preferable if solid industrial residues and by-products could be suitably formulated, processed, and then

returned back to forest ecosystems as a fertilizer / ameliorant or reused, e. g. as an earth construction agent. If we compare the heavy metal concentrations in the studied activated sludge with those reported in the literature for non-contaminated Finnish soil [30], it can be observed (see Table 2), that except for the cadmium concentration, all other metal concentrations in the sludge are in good agreement with the above mentioned values. Although the concentrations of heavy metals in the activated sludge were low, it must be remembered that caution must always be exercised when industrial residue based by-products are applied in the natural environment. Furthermore, although many European countries, e. g. Finland, Sweden, Germany, Spain and France, have established legislation that enables and controls the beneficial use of waste materials via recycling, these controls differ so that the exact local regulatory requirement relating to any existing domestic legislation must always be applied.

Extractable element concentrations in the sludge

If inorganic materials and by-products such as activated sludge or ash are disposed of in landfills, low metal concentrations and the tight binding of elements to the matrix are favourable [32]. When the sequential extraction procedure is applied in the fractionation of metals in environmental samples, the ability of different extraction agents to release metal ions depends on their association with specific fractions in the sample. Extractants such as electrolytes, weak acids and chelating agents release metals from the coordination sites, while strong acids and redox agents are capable

of releasing additional quantities of metals as a result of the decomposition of the solid matrix [8]. Therefore, consecutive extraction techniques allow us to obtain information on the mobility and thus the bioavailability of major and trace elements under different environmental conditions, such as acidic, alkaline, oxidizing or reducing conditions or through the action of a chelating agent [9]. The distribution of analysed elements in the activated sludge after three-stage BCR extraction between acid-soluble (BCR1), reducible (BCR2) and oxidisable (BCR3) fractions is presented in Table 2.

In the acid-soluble fraction (BCR1), which is an exchangeable or non-specifically sorbed fraction, adsorbed elements are retained on the solid surface by relatively weak electrostatic interaction. These elements can be released, for example, by ion-exchange [33–34]. Thus, this fraction represents the most rapidly bioavailable metals, and a reduction in pH could cause remobilization of these metals [9]. Acetic acid, which is used as an extractant in this fraction, is considered to release “exchangeable” elements and to dissolve some poorly crystalline hydroxy- and carbonate-metal phases. It is of major concern that this extraction is as complex as possible, since the pH and its changes are key parameters that determine the potential redistribution of trace elements during extraction [25, 35]. The use of acetic acid as an extractant has been questioned as it does not occur in nature. However, according to Golia et al. [36], acetic acid is found among the natural organic acids secreted by plant roots, so the metals extracted by acetic acid may be similar to the fraction of metals available to the plants. Furthermore, according to Svensson et al. [37], acetic acid is a realistic choice to simulate a plausible worst-case scenario for waste material co-disposed with municipal solid waste. The use of acetic acid as an extractor emulates the organic acids produced from decomposing waste in anaerobic environments such as actively decomposing landfills, since in the acetogenesis phase during the anaerobic degradation of organic matter, carboxylic acids (e. g. acetic acid), volatile fatty acids and ethanol are produced and transformed into acetate, carbon dioxide and hydrogen by acidogenic bacteria [38]. The highest extractable concentrations in this fraction (BCR1) were observed for S (1 650 mg kg⁻¹; d. w.), Mn (523 mg kg⁻¹; d. w.), P (182 mg kg⁻¹; d. w.), Ba (57.9 mg kg⁻¹; d. w.), Zn (55.2 mg kg⁻¹; d. w.) and for Al (13.9 mg kg⁻¹; d. w.). If we disregard elements whose extractable concentrations were lower than the detection limit, only the extractable concentrations of Mn (523 mg kg⁻¹; d. w.), Ni (5.1 mg kg⁻¹; d. w.), S (1 650 mg kg⁻¹; d. w.) and Ti (1.3 mg kg⁻¹; d. w.) in this fraction were higher than those in the reducible (BCR2) fraction. The extractable concentration of Mn in the BCR1 fraction was also higher than that (160 mg kg⁻¹; d. w.) in the BCR2 fraction and that (135 mg kg⁻¹; d. w.) in the BCR3 fraction. If we disregard elements whose concentrations were lower than the detection limit, the partitioning share of the extractable heavy metals for the activated sludge in this fraction was between 0.26% (Fe) and 59.4% (Mn) of the total heavy metal concentrations.

The reducible fraction (BCR2) contained metals associated with Fe-Mn oxides, which can be dissolved by changes in the redox potential [9]. For example, the leaching of some metals, e. g., V, Cr, Fe and As, can significantly depend on the redox conditions [39]. Under disposal conditions, redox reactions can occur as a result of microbiologically mediated processes due to the presence of organic matter or abiotic transformations leading to the formation of reducing gases (H₂) [40]. According to the TOC value (405 mg kg⁻¹; d. w.), the amount of organic material in the sludge was relatively high, and it is therefore possible that the metals in this fraction form complexes with the organic matter [40]. Furthermore, during disposal, biodegradation or the presence of reduced mineral phases can reduce the redox potential. The redox potential directly affects the mobility of trace elements by changing the oxidation state and indirectly by changing the quantity of redox-sensitive metal surfaces [34]. The highest extractable concentrations in this fraction (BCR2) were observed for P (441 mg kg⁻¹; d. w.), S (409 mg kg⁻¹; d. w.), Fe (321 mg kg⁻¹; d. w.), Mn (160 mg kg⁻¹; d. w.), Al (80.9 mg kg⁻¹; d. w.), Ba (63.1 mg kg⁻¹; d. w.) and Zn (66.7 mg kg⁻¹; d. w.). If we disregard elements whose extractable concentrations were lower than the detection limit as well as Ba and Mn, only the extractable concentration of Mn in this fraction was higher than that (135 mg kg⁻¹; d. w.) in the oxidisable (BCR3) fraction. However, the extractable concentration of Ba in this fraction was equal to that (63.1 mg kg⁻¹; d. w.) in the BCR3 fraction. If we disregard elements whose concentrations were lower than the detection limit, the partitioning of the extractable heavy metals for the activated sludge in this fraction was between 4.0% (Cd) and 30.0% (Ba) of the total heavy metal concentrations. This indicates that the heavy metals in the activated sludge are not easily released, for example, by the changes in the redox potential.

The oxidisable fraction (BCR3), which is the fraction after extraction with a combination of H₂O₂/CH₃COONH₄, corresponds to metals that are organically bound or occur as oxidisable minerals, e. g. sulphides [9]. As metals bound to this fraction can be released under oxidising conditions, an oxidation process is usually applied to extract the metals associated with the above-mentioned phase. Hydrogen peroxide (H₂O₂), which is used as an oxidising reagent in this fraction, is a strong oxidant. In general, hydrogen peroxide applied to a heated medium (i. e. 85 °C) is the preferred reagent for dissolving organic matter as a compromise between the complete degradation of organic matter and the minimum alteration of silicates. Heating promotes the oxidation process [9]. Furthermore, hydrogen peroxide also oxidises sulphides to sulphates [33]. Besides the extraction of cations by ammonium ions, partial removal of some elements may occur due to complexation with acetate anions, although ammonium acetate is a weak extractant [41]. Due to the relatively high TOC value of 405 mg kg⁻¹ (d. w.) in the activated sludge, the release of metals and sulphur bound to the organic matter of this residue is possible if conditions become oxidative and

the organic matter degrades. However, according to Smichowski et al. [42], the organic fraction released in the oxidisable step is not considered to be very mobile or available. The highest extractable concentrations in this fraction (BCR3) were observed for S (6660 mg kg⁻¹; d. w.), P (2270 mg kg⁻¹; d. w.), Al (2680 mg kg⁻¹; d. w.) and Fe (2110 mg kg⁻¹; d. w.). If we disregard elements whose concentrations were lower than the detection limits, as well as Ba and Mn, the extractable concentrations of other element in this fraction (BCR3) were higher than those in the BCR1 and BCR2 fractions. Furthermore, if we disregard elements whose concentrations were lower than the detection limits, the partitioning of the extractable heavy metals for the activated sludge in this fraction was between 15.3% (Mn) and 90.5% (Al) of the total heavy metal concentrations.

If we disregard elements, whose concentrations were lower than the detection limits, it can be seen that the recovery values (R% values) of elements varied between 81.6% (Ni) and 96.4% (V). This indicates the ratio of sum of BCR sequential extraction procedure to the total digestion using the USEPA method 3051A. Although this ratio was very high for most of the element in the activated sludge, the BCR sequential extraction procedure used in this study illustrates the worst-case environmental scenarios in which the components of the sample become soluble and mobile [9]. However, in this context we would like to point out that caution must always be exercised when activated sludge or other industrial residues are utilized and the existing legislation must always be applied.

CONCLUSIONS

According to the three-stage sequential extraction procedure, in which elements in the activated sludge were fractionated between acid-soluble (CH₃COOH; BCR1), reducible (NH₂OH-HCl; BCR2) and oxidisable (H₂O₂ + CH₃COONH₄; BCR3) fractions, the highest extractable concentrations for most of the heavy metals occurred in the BCR3 fraction, although the metals in the activated sludge were extractable in all fractions. The highest extractable concentrations in the BCR1 fraction were observed for S (1650 mg kg⁻¹; d. w.), Mn (523 mg kg⁻¹; d. w.), P (182 mg kg⁻¹; d. w.), Ba (57.9 mg kg⁻¹; d. w.), Zn (55.2 mg kg⁻¹; d. w.) and Al (13.9 mg kg⁻¹; d. w.). If we disregard elements whose extractable concentrations were lower than the detection limit, only the extractable concentration of Mn, Ni (5.1 mg kg⁻¹; d. w.) and S in this fraction were higher than those in the reducible (BCR2) fraction. However, the extractable concentration of Mn in this fraction was also higher than that (135 mg kg⁻¹; d. w.) in the oxidisable (BCR3) fraction. The partitioning share of the extractable heavy metals for the activated sludge in the BCR1 fraction was between 0.26% (Fe) and 59.4% (Mn) of the total heavy metal concentrations. This indicates that the heavy metals in the activated sludge are not easily released, for example, by ion-exchange.

The highest extractable concentrations in the BCR2 fraction were observed for P (441 mg kg⁻¹; d. w.), S (409 mg kg⁻¹; d. w.), Fe (321 mg kg⁻¹; d. w.), Mn (160 mg kg⁻¹; d. w.), Al (80.9 mg kg⁻¹; d. w.), Ba (63.1 mg kg⁻¹; d. w.) and Zn (66.7 mg kg⁻¹; d. w.). If we disregard elements whose extractable concentrations were lower than the detection limit, only the extractable concentration of Mn in this fraction was higher than that (135 mg kg⁻¹; d. w.) in the oxidisable (BCR3) fraction. However, the extractable concentration of Ba in this fraction was equal to that (63.1 mg kg⁻¹; d. w.) in the BCR3 fraction. If we disregard elements whose concentrations were lower than the detection limit, the partitioning of the extractable heavy metals for the activated sludge in this fraction was between 4.0% (Cd) and 30.0% (Ba) of the total heavy metal concentrations. This indicates that the heavy metals in the activated sludge are not easily released, for example, by the changes in the redox potential.

From the environmental point of view, the metals bound to the BCR3 fraction are not considered to be very mobile or available. The highest extractable concentrations in this fraction (BCR3) were observed for S (6660 mg kg⁻¹; d. w.), P (2270 mg kg⁻¹; d. w.), Al (2680 mg kg⁻¹; d. w.) and Fe (2110 mg kg⁻¹; d. w.). If we disregard elements whose concentrations were lower than the detection limits, as well as Ba and Mn, the extractable concentrations of other element in this fraction (BCR3) were higher than those in the BCR1 and BCR2 fractions. Furthermore, if we disregard elements whose concentrations were lower than the detection limits, the partitioning of the extractable heavy metals for the activated sludge in this fraction (BCR3) was between 15.3% (Mn) and 90.5% (Al) of the total heavy metal concentrations. Therefore, we conclude that, if the activated sludge investigated in this study is used as a potential soil conditioning and improvement agent, the metals in the sludge are not likely to be dissolved easily under the conditions normally found in nature.

Although the highest extractable concentrations of most of the metals occurred in the BCR3 fraction, the recovery values (R% values), which are the ratio of the sum of the BCR sequential extraction procedure to the total digestion using the USEPA method 3051A, varied between 81.6% (Ni) and 96.4% (V). Due to high R% values for certain elements we would like to point out that caution must always be exercised when activated sludge is utilized and the existing legislation must always be applied.

ACKNOWLEDGEMENTS

The authors wish to thank the technical staff of Suomen Ympäristöpalvelu Oy, who kindly conducted all the chemical analyses. They also want to express their gratitude to Mr Olli Taikina-Aho at the Institute of Electronic Optics, University of Oulu, for the XRD data, and to Dr Roy Siddall for correcting the English language.

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**BCR PAKOPINĖS EKSTRAKCIJOS PROCEDŪROS
NAUDOJIMAS ELEMENTŲ FRAKCIONAVIMUI
PULPOS IR POPIERIAUS MALIMO AKTYVUOTAME
DUMBLE**

S a n t r a u k a

Straipsnyje pateikiami duomenys apie elementų frakcionavimą tarp trijų pulpos ir popieriaus malimo aktyvuoto dumblo frakcijų.