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FIBER SLUDGE AS A BIOADSORBENT FOR CATION REMOVAL FROM INDUSTRIAL WASTEWATERS

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ABSTRACT

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The topic of the thesis concerns reutilization of fibre sludge waste to remove metals from industrial wastewater. The main objective of the thesis was to discover if such application is possible. The focus was kept on the properties of fibre sludge and on the issues affecting adsorption. The thesis is theory-based. And the primary research method used primarily was literature review. The articles used in the thesis are based on the laboratory studies. The adsorption experiments were conducted using the stock solutions. Three kinds of fibre sludge – based adsorbents were studied. They were the original non-modified fibre sludge, fibre sludge subjected to slow pyrolysis, and chemically activated fibre sludge. The impact of the pretreatment methods and adsorption parameters was evaluated. The fibre sludge samples used in each of the three cases resulted from different feedstocks and pulping processes. Therefore, the obtained conclusions are specific for each of the three cases concerned in the thesis.

It was found that the fibre sludge can adsorb metals from aqueous solutions without being chemically activated. The metals adsorbed are Pb, Ni, Cd, Co. The adsorption yield was over 70% for all the metals within the pH range from 2 to 5. The best pH for the adsorption was 4.5. The best biomass concentration was 1%. Concerning the contact time, 70%-89% of all the four metals were adsorbed within 15 min. The surface area was mentioned as a significant parameter. The chemically activated fibre sludge adsorbed the following metals Cu, Co, Ni , Cr, Zn. The pH of adsorption was 6.2. The adsorption yield of 93% was achieved within 10 s for all the five metals. The pyrolyzed fibre sludge was analyzed but not experimentally tested as adsorbent. Based on the analyses the following conclusions were reported. The material from the same factory is homogeneous unlike the samples from different factories. High inorganic content in fibre sludge was reported to reduce mechanical strength of granular adsorbent produced from fibre sludge. The laboratory studies described in the thesis report fibre sludge to be a suitable and even commercially competitive material for metal adsorption from water. Therefore, industrial scale experiments using real wastewater are to be conducted to prove the reliability of fibre sludge to be an adsorbent or its precursor.

Key words
Activated, fibre sludge, metal adsorbent, non-modified, pyrolyzed.

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1 INTRODUCTION

Fibre sludge is a waste produced in large amounts annually. Due to its organic content the sludge is not allowed to be landfilled anymore. Therefore, new waste management methods are researched to deal with fibre sludge. According to the waste hierarchy the primary option of waste management is reuse. The aim of this thesis is to gather information about fibre sludge as a metal adsorbent in industrial wastewaters. The limitations of this study are as follows. The thesis is a literature review based on the laboratory scale experiments reported. The topic is very specific and not yet widely researched. Therefore, not many studies concerning fibre sludge as a metal adsorbent were found in literature. No cases of industrial scale applications of fibre sludge adsorbents were found. And no laboratory experiments regarding the topic were conducted by the thesis author herself.

The objective of this study was to answer the following questions. Does fibre sludge work as a metal adsorbent? Does fibre sludge adsorb metals without being activated or modified? Which metals adsorb better? What are the key parameters affecting adsorption? In terms of industrial scale application, what process conditions affect adsorption? Among the personal objectives of the thesis author were to learn what is fibre sludge and how it is formed, and why it should be researched nowadays. The author aimed to understand the bonding principles between fibre sludge and metals. Three cases of adsorption are considered in the thesis. They concern the original, non-modified, fibre sludge, the pyrolyzed fibre sludge, and chemically activated fibre sludge. The primary interest was the non-modified fibre sludge. After the adsorption overview, the effect of various parameters on adsorption was evaluated. The affecting issues include, pH, biomass (fibre sludge) concentration in water, initial metal concentration in water, contact time, surface area, temperature, pressure and functional groups. After the investigation of the impacting parameters, the overall conclusions of the literature review are drawn.

2 FIBRE SLUDGE IS ACTIVELY RESEARCHED

In this chapter the basic facts about fibre sludge are gathered. They concern origin, chemical composition and properties of this material. The origin refers to the feedstock material and pulping technology used in pulp and paper production. The chemical composition includes both organic and inorganic content of fibre sludge. Fibre sludge have been actively researched over the past few years. One of the reasons is a number of legislative changes concerning fibre sludge disposal. A detailed analysis of physico - chemical properties of fibre sludge is described in this chapter. The properties of fibre sludge include porosity, homogeneity, moisture level, and ash content, etc... The analysis allowed researchers to determine potential applicability of fibre sludge as a metal adsorbent.

2.1 Fibre sludge

Fibre sludge is also known as primary sludge (Devi & Saroha 2016, 17). It is a waste product of pulp and paper process. The pulping process flow chart is presented in Figure 1. The units where fibre sludge is obtained from can be also seen from the figure. The material processing starts at the debarking unit. The wood is then chipped. The obtained wood chips are subjected to cooking. After that the pulp is bleached and dried. The by-product of the bleaching process is wastewater. The wastewaters from pulp bleaching and drying steps contain fibre sludge (Holm 2013, 25). According to Figure 1 the fibre sludge is then collected into the processing unit. Bark sludge and bio sludge are also formed during the pulping process. However, they are not considered in this thesis.

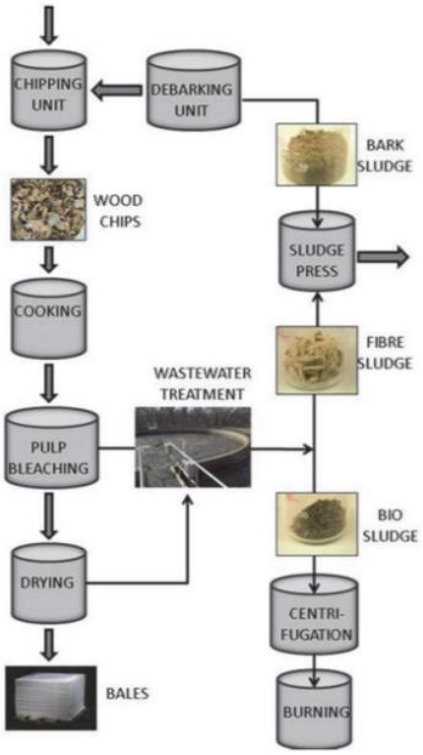

FIGURE 1. Process flow sheet at the pulp mill (Holm 2013, 25)

The fibre sludge is to be extracted from water before further processing. Figure 2 provides a more detailed view on how the fibre sludge is collected from the pulping wastewater. Figure 2 represents the wastewater treatment process chart of a pulp-and-paper factory. The wastewater from the pulping process is passed through primary and secondary clarifiers for purification. During clarification the sludge is separated from water and exits the clarifiers as primary and secondary residual correspondingly. The sludge is then combined and dried in a dewatering unit. The water obtained from the dewatering unit is recycled back into the process. And the dewatered sludge is collected for further processing. According to Naik and Moriconi, fibre sludge is obtained as primary residual by means of sedimentation or dissolved air flotation (FIGURE 2). (Naik & Moriconi 2005, 7.)

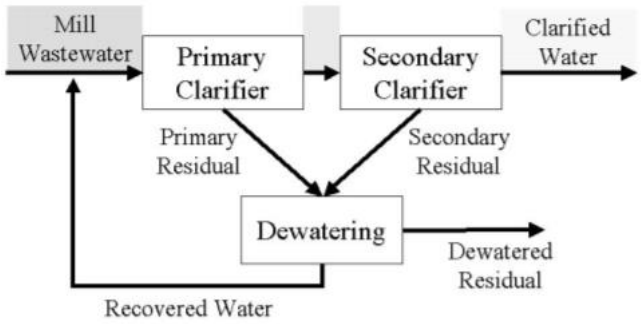

FIGURE 2. Pulp and paper mill wastewater treatment process (Naik & Moriconi 2005, 7)

The secondary residual does not refer to fibre sludge and remains outside the scope of this thesis. The general composition of fibre sludge is presented in Table 1. Fibre sludge contains mostly cellulose and hemicellulose (TABLE 1) and has a small share of inorganic components or ash (Table 1, Table 2). Fibre sludge can also contain the residues of lignin and cooking chemicals. (Holm et al. 2013, 433.) The composition of fibre sludge depends on the pulp mill and the chemical pulping process. The fibre sludge considered in Jana Holm's doctoral thesis has the following background. The sludge was obtained from Nordic pine, spruce, and birch feedstock, and processed using Kraft pulping process. (Holm 2013, 15.) The Kraft technology implies cooking of the wood chips in NaOH + Na_2S (Holm 2013, 25).

TABLE 1. Composition of fiber sludge (Holm 2013, 41 [Tappi Standard T 203 cm-09 - Alpha-, Beta- and Gamma-Cellulose in Pulp 2009]; Holm, Lassi & Hernoux-Villiere 2013, 233)

COMPOSITION OF FIBRE SLUDGE	
Organic matter content	80-85%
Cellulose	93-94%
Hemicellulose	6-7%
Inorganic matter content	~ 20%

Due to this process, fibre sludge has a very low lignin content (Holm 2013, 26). Table 2 presents elemental analysis of the fibre sludge researched in Jana Holm's study. The shortenings "n.d." and "d.s." in the table mean "non-determined" and "calculated from the dry material (substance)" correspondingly. As the Table 2 shows, the highest share in the dried fibre sludge belongs to organic components. Almost 40% of the fibre sludge content is carbon. The amount of oxygen was not determined. The amount of hydrogen is close to 5%. The sludge includes nearly 20% of ash. The elemental composition of the ash was not revealed in Jana Holm's work. The residues of cooking chemicals are also traced in the sludge. The quantities of nitrogen and sulfur are less than 0.5% (Holm et al. 2013, 433.)

TABLE 2. Elemental analysis and some physical properties of fibre sludge. (Holm et al. 2013, 433)

ELEMENTAL ANALYSIS AND SOME PHYSICAL PROPERTIES OF FIBRE SLUDGE	
Carbon %, ds	38.4
Hydrogen %, d.s.	4.7
Oxygen %	n.d.
Nitrogen d.s.	0.3
Sulfur %, d.s.	<0.5
Heat Value (MJ/Kg), d.s.	13
Moisture %, as received	~ 50
Ash cotent %, d.s.	20.7

However, another group of researchers conducted a similar study in Sweden. As a result of their research they have published quite detailed composition of the ash (Phyllis2 2020 [Svärd & Eskilsson 2001]). The study was conducted at Technical Research Institute of Sweden. And the sludge sample was obtained from pulp plant in Vargön, Sweeden. The fuel properties are listed in Table 3. And the chemical composition is outlined in Table 4. The values are sorted into three groups named "Ar", "Dry", and "Daf". The shortenings mean the following. "Ar" stands for "as received", that is the material in its original form including moisture and ash. The dry materials with and without ash are marked as "Dry" and "Daf" correspondingly. (Phyllis2 2020 [Svärd & Eskilsson 2001]).

TABLE 3. Fuel properties of fibre sludge (Nilsson 2009 [Svärd & Eskilsson 2001])

FUEL PROPERTIES				
Proximate Analysis	**Unit**	**Value**		
		Ar	**Dry**	**Daf**
Moisture content	wt%	4,60		
Ash content at 550°C	wt%	29,76	31,20	
Ultimate Analysis				
Carbon	wt%	32,05	33,60	48,84
Hydrogen	wt%	4,10	4,30	6,25
Nitrogen	wt%	1,24	1,30	1,89
Sulphur	wt%	1,34	1,40	2,03
Oxygen	wt%	25,38	26,60	38,66
Total (with halides)	wt%	98,63	98,56	97,91
CALORIFIC VALUES				
Net calorific value (LHV)	MJ/kg	12,15	12,85	18,68
Gross calorific value (HHV)	MJ/kg	13,15	13,78	20,03
HHVMilne	MJ/kg	12,94	13,56	19,71

It is noticeable that the ultimate analysis data in Table 3 is quite near to the elemental analysis results in Table 2. Carbon content in Finnish fibre sludge is only 4.8 wt% higher than the content in Swedish samples. The difference in hydrogen content in dried samples is only 0.4 wt%. Nitrogen content in Nilsson's samples is 1 wt% higher than in Finnish fibre sludge. Swedish fibre sludge smples also contained more sulfur than the finnish samples. The difference is more than 0.9 wt%. This content similarities are probably because Finnish and Swedish pulp mills use similar feedstocks, the Nordic trees. Therefore, the ash considered in Jana Holm's study in Finland (TABLE 2) might have same or similar content discovered by Nilsson's team in Sweden (TABLE 4). Table 4 outlines the elements contained in the fibre sludge ash considered in Nilsson's study.

TABLE 4. Chemical content of fibre sludege (Nilsson 2009 [Svärd & Eskilsson 2001])

CHEMICAL ANALYSES				
Halides	**Unit**	**Value**		
		Ar	**Dry**	**Daf**
Chlorine (Cl)	mg/kg	1 526,4	1 600,0	2 325,6
MAJOR ELEMENTS				
Aluminium (Al)	mg/kg (dry)	81 900,0		
Potassium (K)	mg/kg (dry)	4 500,0		
Sodium (Na)	mg/kg (dry)	3 100,0		
Calcium (Ca)	mg/kg (dry)	5 900,0		
Silicon (Si)	mg/kg (dry)	56 400,0		
Magnesium (Mg)	mg/kg (dry)	4 300,0		
Iron (Fe)	mg/kg (dry)	4 300,0		
Phosphorus (P)	mg/kg (dry)	2 800,0		
Titanium (Ti)	mg/kg (dry)	2 900,0		
MINOR ELEMENTS				
Arsenic (As)	mg/kg (dry)	13,0		
Cadmium (Cd)	mg/kg (dry)	0,5		
Cobalt (Co)	mg/kg (dry)	3,0		
Chromium (Cr)	mg/kg (dry)	52,0		
Copper (Cu)	mg/kg (dry)	20,0		
Manganese (Mn)	mg/kg (dry)	100,0		
Nickel (Ni)	mg/kg (dry)	23,0		
Lead (Pb)	mg/kg (dry)	7,0		
Vanadium (V)	mg/kg (dry)	30,0		
Zinc (Zn)	mg/kg (dry)	69,0		
Barium (Ba)	mg/kg (dry)	<100		
Molybdenium (Mo)	mg/kg (dry)	2,0		

As it was mentioned above, these elements are not in the fibre sludge itself. They rather represent the ash, which is a part of fibre sludge (Lassi 2020). According to the data, the biggest share in the ash belongs to aluminium and silicon. The other major elements in the fibre sludge ash are calcium, potassium, iron, magnesium, sodium, titanium, and phosphorus. The ash also contains a wide variety of metals among its minor elements. According to another literature source carbonates may be present in fibre sludge. And the carbonates can activate the surface of an adsorbent, if they are alkali-metal carbonates. (Viswanathan, Neel & Varadarajan 2009, 43.) However, such activation may occur only in the case, when the ash is not removed during the adsorbent preparation (Lassi 2020.)

2.2 Legislative changes in disposal of fibre sudge

According to Moriconi and Naik in USA only 25% of fiber sludge is utilized in some way. The other 25% is incinerated and the remaining 50% of it is landfilled. (Naik & Moriconi 2005, 7.) In Finland 750 000 tons of wet fiber sludge are generated each year. In the past years most of the sludge had been usually incinerated and landfilled as in US. (Kuokkanen, Mäentausta & Kuokkanen 2018, 1457.) However, the new EU policy brought the new concept of the waste hierarchy. The prior position in the hierarchy belongs to prevention of waste formation. The next favorable options are waste reusage followed by waste recycling, energy recovery, incineration. The hierarchy list is closed by landfilling. In practical application the primary goal for the industries became to reuse or recycle the sludge. Their secondary goal was to utilize the sludge as an energy source. The disposal of waste was the least preferred option. (Kuokkanen, Mäentausta & Kuokkanen 2018, 1458.)

The new waste hierarchy was supported by a taxation policy. Starting from 2010 fibre sludge has been subjected to tax. The rate has been rising over time as follows. The tax for the landfilled waste was 40€ per ton before the year 2013. Starting from the year 2013 the tax was set to 50 euros per ton. (Waste Tax Act 2010/1126 (original act).) And from the year 2016 the rate was raised to 70 euros per ton. (Waste Tax Act 2010/1126 (updated act)). Thus, at the annual output of 750 000 tons of fibre sludge and the tax rate of 70 eouros per ton, the landfills' operators were to pay around 52.5 million euros each year. And nowadays, according to the updated Decree on Landfills 331/2013, landfilling of fibre sludge is not allowed in Finland anymore, as the organic content in fibre sludge is more than 10% (Decree on landfills 331/2013). Therefore, fibre sludge has been a subject of an active research over the past few years. This thesis is focused on utilization of fibre sludge as a metal adsorbent for industrial wastewater treatment.

2.3 Physicochemical properties of fibre sludge

A research was conducted to determine the physicochemical properties of fibre sludge (FS). By these properties the researches managed to conclude on applicability of the sludge as a raw material for adsorbent production. The fibre sludge samples were obtained from two factories, marked "F1", "F2". Both factories used Eucalyptus globulus wood as their feedstock and Kraft process as their pulping technology. The pyrolyzed samples were marked with letter "P". Some of the pyrolyzed samples were also acid-washed. They were marked "PW". All the samples were studied via proximate analysis. They were

also analysed for total organic carbon (TOC) and inorganic carbon (IC) determination. In addition to the mentioned procedures, the samples also went under an attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The specific surface area (SBET) and porosity of the samples were obtained via N_2 adsorption isotherms. (Jaria, Silva, Ferreira, Otero & Calisto 2016, 203.)

Let us first consider the results of the ATR-FTIR analysis (APPENDIX 1). The samples' names are to be interpreted as follows. The sample F1PS2-PW is the second sample (2) of primary sludge (PS) obtained from factory 1 (F1), which was pyrolyzed (P) and acid-washed (W) for the experiment. Four samples were taken from each factory and dried. The analysis was conducted for the samples first after drying, then after pyrolysis. The pyrolysis was followed by acid washing. The washed samples were also analysed. (Jaria et al 2016, 204.) According to the data the pyrolyzed samples have less peaks than the original samples (APPENDIX 1). The chemical composition of the raw fibre sludge is much more complex than that of the pyrolyzed and acid-washed sludge (Jaria et al 2016, 206). Low variability between the samples of one factory was also noticed by the researchers. And low variability means that the sludge is a homogeneous and consistent material. Therefore, it was concluded to be a reliable raw material for an adsorbent production. (Jaria et al 2016, 203-207.)

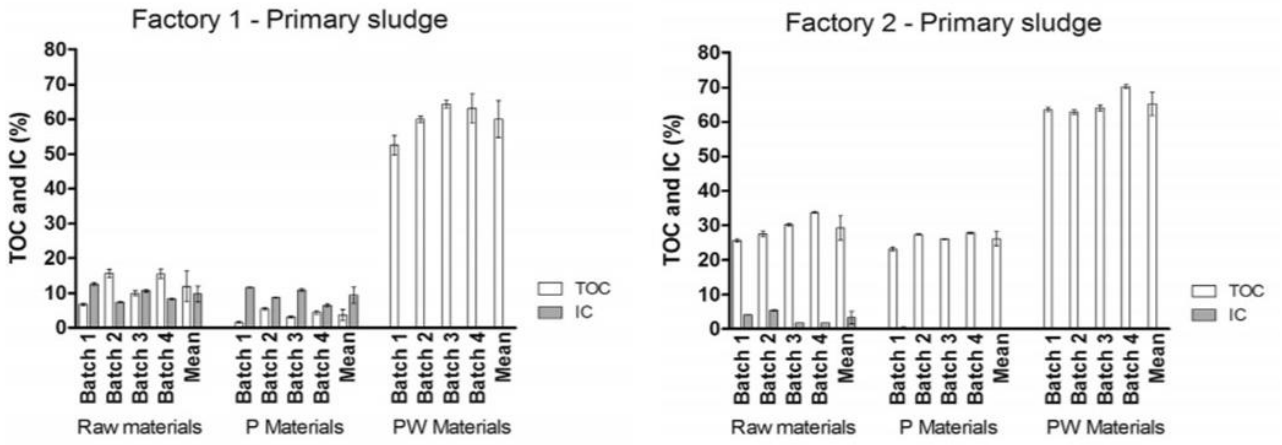

FIGURE 3. Inorganic carbon (IC, %) and total organic carbon (TOC, %) (obtained by difference between total carbon (TC, %) and IC) for raw, pyrolyzed (P) and pyrolyzed and washed (PW) materials (n=3), for the four batches of primary sludge (PS) (Jaria, Silva, Ferreira, Otero & Calisto 2016, 205)

Figure 3 and Table 5 present information about inorganic carbon and total organic carbon content in fibre sludge batches of two factories. The raw samples from factory 1 (F1) contain more inorganic carbon (IC) than the raw samples from factory 2 (F2). And the raw samples from F2 have higher level of total organic carbon (TOC) than the raw samples of F1. Interestingly, the pyrolysis has not affected the amount of IC in samples F1. And in samples of F2 no IC is traced after pyrolysis. A slight reduction of

the total organic carbon (TOC) as a result of pyrolysis is visible from the data. However, after the acid washing the TOC increased significantly. The numbers in the table show, that the acid washing has almost fully removed the inorganic carbon (IC) from the fibre sludge. (Jaria, Silva, Ferreira, Otero & Calisto 2016, 205.)

TABLE 5. Total (TC, %) and inorganic carbon (IC, %) values (n = 3) for raw, P and PW materials. TOC was obtained by difference. (Jaria, Silva, Ferreira, Otero & Calisto 2016 [supplementary data, S8])

Raw Materials	**TC (%)**	**IC (%)**	**TOC (%)**	**P Materials**	**TC (%)**	**IC (%)**	**TOC (%)**	**PW Materials**	**TC (%)**	**IC (%)**	**TOC (%)**
F1PS1	19.5 ± 0.2	12.6 ± 0.3	6.8 ± 0.3	F1PS1-P	13.4 ± 0.1	11.7 ± 0.1	1.7 ± 0.2	F1PS1-PW	53 ± 3	0.140 ± 0.001	53 ± 3
F1PS2	23 ± 1	7.4 ± 0.2	16 ± 1	F1PS2-P	14.3 ± 0.4	8.80 ± 0.04	5.5 ± 0.4	F1PS2-PW	59.0 ± 0.9	0.014 ± 0.003	60.0 ± 0.9
F1PS3	20.8 ± 0.7	10.7 ± 0.4	10.0 ± 0.7	F1PS3-P	14.1 ± 0.2	10.9 ± 0.3	3.2 ± 0.3	F1PS3-PW	64 ± 1	0.024 ± 0.001	64 ± 1
F1PS4	24 ± 1	8.4 ± 0.2	15 ± 1	F1PS4-P	11.0 ± 0.2	6.5 ± 0.5	4.5 ± 0.5	F1PS4-PW	63 ± 4	0.10 ± 0.02	63 ± 4
F2PS1	29.8 ± 0.3	4.1 ± 0.1	25.7 ± 0.4	F2PS1-P	23.3 ± 0.1	0.05 ± 0.53	23.2 ± 0.5	F2PS1-PW	63.6 ± 0.6	0.019 ± 0.002	63.6 ± 0.6
F2PS2	32.9 ± 0.8	5.4 ± 0.2	27.5 ± 0.8	F2PS2-P	27.4 ± 0.2	0.021 ± 0.002	27.4 ± 0.2	F2PS2-PW	63.0 ± 0.7	0.013 ± 0.001	62.9 ± 0.7
F2PS3	32 ± 2	1.77 ± 0.03	30.2 ± 0.4	F2PS3-P	26.4 ± 0.1	0.22 ± 0.01	26.1 ± 0.1	F2PS3-PW	64.0 ± 0.9	0.013 ± 0.003	64.0 ± 0.9
F2PS4	35 ± 2	1.752 ± 0.002	33.8 ± 0.2	F2PS4-P	27.9 ± 0.2	0.03 ± 0.05	27.8 ± 0.2	F2PS4-PW	70.2 ± 0.6	0.010 ± 0.001	70.2 ± 0.6

Pyrolysis and acid washing did not impact the chemical composition alone. They have also influenced the surface area and the pore size of the fibre sludge. The data characterizing the pore size and surface area of the pyrolyzed and acid-washed sludge is presented in Table 6. Unfortunately, no information about the surface area and the pore size of the original, the non-pyrolyzed fibre sludge was provided in Jaria´s study. The zero-sample is missing. Therefore, no conclusions on the adsorption ability of the raw non-modified fibre sludge can be made based on the data in Table 6 . It is noticeable that acid washing increases the porosity and surface area of the fibre sludge significantly. Based on the obtained data the pore size and surface area of the P material was concluded to have no adsorptive potential (Jaria, Silva, Ferreira, Otero & Calisto 2016, 205).

TABLE 6. Textural parameters of the P and PW materials (S_{BET} – BET surface area; W_o – micropore volume). (Jaria, Silva, Ferreira, Otero & Calisto 2016 [supplementary data, S9])

	P materials		PW materials	
Sample	S_{BET} ($m^2\ g^{-1}$)	W_0 ($cm^3\ g^{-1}$)	S_{BET} ($m^2\ g^{-1}$)	W_0 ($cm^3\ g^{-1}$)
F1PS1	4.2 ± 0.4	0.0000	413 ± 3	0.0149

(continues)

TABLE 6. (continues)

F1PS2	**11.8 ± 0.4**	**0.0000**	**488 ± 2**	**0.0336**
F1PS3	9.1 ± 0.3	0.0000	399 ± 1	0.0529
F1PS4	39.7 ± 0.2	0.0059	387 ± 3	0.0837
F2PS1	107 ± 1	0.0154	236 ± 2	0.0454
F2PS2	96 ± 1	0.0233	343 ± 5	0.0000
F2PS3	94 ± 1	0.0147	292 ± 1	0.0460
F2PS4	83.0 ± 0.5	0.0226	337 ± 2	0.0290

Therefore, acid-washing is viewed as a vital step after pyrolysis in the process of the adsorbent production. (Jaria, Silva, Ferreira, Otero & Calisto 2016, 207-208.) But despite the mentioned advantages the acid washing appeared to have serious drawbacks also. The production yield of the carbon product from the acid washed sludge was as low as 4%. High IC content also reduces hardness and strength of the adsorbent material. Therefore, it was impossible to produce granular adsorbent that could withstand the adsorption. The granules would fall apart. This fact is presented to be a disadvantage in Jaria's study. However, Alhuwalia, another researcher investigating the adsorption properties of fibre sludge, expressed another opinion. He stated that the smaller the size of the particle is, the bigger the surface area is, hence, the better is the adsorption. Some people even pulverize their samples to improve the adsorption, according to Alhuwalia. A small particle size in Jaria's study is not good for adsorption due to the mechanical aspects of the adsorption process design. Too small adsorbent particles might pass together with the water. And in that case, filtration unit is to be added to the process, which would be an additional expense for the factory. (Rahikka 2020.) For the process that does not include filtration, mechanical strength of the adsorbent should be enough to withstand high flow volumes and rates (Lassi 2020).

The moisture, volatile matter, and ash content were determined in raw and acid-washed samples via proximate analysis. (Jaria, Silva, Ferreira, Otero & Calisto 2016, 205.) The results are presented in Table 7. According to this data acid washing raised the moisture level of the pyrolyzed samples by 9 wt% in samples from F1 and by 4.5 wt% in samples from F2. Acid washing also increased the fixed carbon content roughly by 50 wt% in samples from factory 1 and by 59 wt% in samples from factory 2. Interestingly, the sludge from factory 1 has nearly twice as much ash as the sludge from factory 2. After pyrolysis and acid washing the amount of ash decreased in samples from both factories. Interestingly, the amount of ash after pyrolysis and acid washing is nearly same in both F1- and F2-samples regardless the initial ash content in raw samples.

TABLE 7. Proximate analysis (wt%, dry basis) for raw and PW materials. (Jaria, Silva, Ferreira, Otero & Calisto 2016 [supplementary data, S10])

	Raw Materials				PW Materials			
Sample	**Moisture content**	**Ash**	**Volatile Matter**	**Fixed Carbon**	**Moisture content**	**Ash**	**Volatile Matter**	**Fixed Carbon**
F1PS1	0.9	55.5	44.8	0.0	12.0	22.4	18.0	59.5
F1PS2	3.1	42.6	56.9	0.5	9.6	26.2	16.6	57.2
F1PS3	1.5	47.3	52.3	0.4	8.0	25.4	12.4	62.2
F1PS4	1.5	42.4	55.3	2.30	13.5	12.7	18.7	68.7
Mean ± SD	*2 ± 1*	*47 ± 6*	*52 ± 5*	*1 ± 1*	*11 ± 2*	*22 ± 6*	*16 ± 3*	*62 ± 5*
F2PS1	4.4	25.6	67.1	7.3	7.2	24.7	7.6	67.7
F2PS2	4.4	25.9	70.6	3.5	4.4	24.8	7.2	68.0
F2PS3	4.9	26.3	64.7	8.9	9.5	23.7	11.2	65.2
F2PS4	3.6	26.6	66.0	7.5	5.1	22.6	18.0	59.3
Mean ± SD	*2.5 ± 0.5*	*26.1 ± 0.4*	*67 ± 3*	*7 ± 2*	*7 ± 2*	*24 ± 1*	*11 ± 5*	*65 ± 4*

It is noticeable that the amount of ash in the samples from factory 1 decreased roughly by half after the acid wash (TABLE 7). However, the amount of ash in the samples from factory 2 has barely changed after the acid wash. Based on their research results Jaria's research team concluded that fibre sludge has a good potential to be used as raw material for adsorbent production. The feasibility of the fibre sludge-based adsorbent depends on how well this material keeps its mechanical and chemical stability over time. It is also important to consider variability of the sludge content among the supplying factories. Combining fibre sludge from different factories into one feedstock for the adsorption production might negatively impact the properties of the adsorbent. (Jaria, Silva, Ferreira, Otero & Calisto 2016, 209.)

3 FIBER SLUDGE AS AN ADSORBENT FOR CATIONS

This chapter describes the adsorption efficiency of the original and modified fibre sludge. Among the modification methods covered in the thesis are pyrolysis and chemical activation with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). The possibility of obtaining magnetic properties by fibre sludge via slow pyrolysis is discussed. Concerning the chemically activated fibre sludge, kinetic study is presented. The experiments on recycling the adsorbent are reported. The adsorption experiments with fibre sludge in its original state are also described in this chapter. By the original state the absence of chemical activation is meant. The kinetic study of those experiments is provided. Principles of bonding between the adsorbent and metals in all three cases are discussed.

3.1 Effect of slow pyrolysis on fibre sludge adsorption properties

According to Devi and Sahora, the adsorption efficiency of sludge-based adsorbents is affected by pretreatment methods and activation conditions. One of the common pretreatment methods is pyrolysis. The type and conditions of pyrolysis impact the form of the product, which can be biogas, biooil, and biochar. Pyrolysis can be slow, fast or flush. Among the three the slow pyrolysis favors the yield of biochar. (Jahirul, Rasul, Chowdhury & Ashwath 2012, 4956.) According to the research findings, adsorption is better at higher temperature of pyrolysis. The reason is that the increase in pyrolysis temperature enlarges the surface area and increases porosity of the adsorbent. However, the studies also show that same adsorption properties are achieved at low temperature of pyrolysis and over a longer time. (Devi & Saroha 2016, 18.)

Concerning fibre sludge as a feedstock for pyrolysis, the following information was found. Callisto, Ferreira and their colleagues have conducted a research, where they studied, how well the pyrolized fibre sludge adsorbs citalopram from water. The highest adsorption capacity was obtained when pyrolyzing the fibre sludge at 800℃ during 150 min at the heat rate of 10℃/min under N_2 saturated atmosphere. The pyrolysis yield in this case was 34%. (Callisto, Ferreira, Santos, Gil, Otero & Esteves 2014, 335-338.) This yield is much better compared to the 4% obtained during Jaria's and Silva's study described in Chapter 2.3. Moreover, it was found that the solid charcoal yield is higher at lower temperatures of pyrolysis. As concluded in Callisto's article, the charcoal yield of the 800℃ pyrolysis was 34%,

and the yield of 315℃ pyrolysis was 58%. (Callisto, Ferreira, Santos, Gil, Otero & Esteves 2014, 338.) The 58% pyrolysis yield in Calisto's study was the highest compared to other results found in literature. The type of pyrolysis producing such a high yield was not mentioned in Calisto's article. Therefore, an additional literature review was conducted to clarify the type of pyrolysis in their research. Another group of researchers, Jahirul and his team, have classified pyrolysis process into slow, fast, and flash based on the heat rate, temperature range and residence time. Their estimations are summarized in Table 8 below.

TABLE 8. Typical operating parameters and products of pyrolysis process. (Jahirul, Rasul, Chowdhury & Ashwath 2012, 4956 [Balat, Balat, Kirtai & Balat 2009; Briggwater 2007])

Pyrolysis process	**Solid residue time (s)**	**Heating rate (K/s)**	**Particle size (mm)**	**Temperature (K)**	**Product Yield (%)**		
					Oil	Char	Gas
Slow	450-550	0.1-1	5-50	550-950	30	35	35
Fast	0.5-10	10-200	<1	850-1250	50	20	30
Flash	<0.5	>1000	<0.2	1050-1300	75	12	13

According to Table 8, the Callisto's pyrolysis with temperatures 800℃ and 315℃ would refer to flash pyrolysis and slow pyrolysis correspondingly (Jahirul, Rasul, Chowdhury & Ashwath 2012, 4956 [Balat, Balat, Kirtai & Balat 2009; Briggwater 2007]). Saleh Al Arni is another researcher who also studied the effect of pyrolysis on biomass. In his study a conventional or slow pyrolysis was conducted at the following conditions. The temperature was 853 K. The heat rate was 45-50℃/min. And the residence time was about 1 hour. Also, in Arni's study several slow pyrolysis experiments were conducted in the temperature range of 663-1253 K. The temperature used in Callisto's study falls in the range of slow pyrolysis temperature in Arni's research. And the heat rate used in Callisto's study is even lower than rate in Arni's research. And the residence time of 150 min in Callisto's study is longer than both the typical slow pyrolysis time mentioned in Jahirul's publication (TABLE 8) and the residence time in Arni's experiments. Therefore, based on Jahirul's and Arni's conclusions, the pyrolysis in Callisto's experiment might be referred to slow pyrolysis.

According to Jahirul's publication, one advantage of pyrolysis as good pretreatment method for the paper mill sludge is possibility to obtain renewable energy from it. The pyrolysis of pulp and paper mill sludge using CO_2 as a reaction medium produces syngas alongside with the magnetic highly alkaline biochar. According to Jahirul's findings, slow pyrolysis produces the highest yield of syngas (Jahirul et al. 2012,

4956). This conclusion was made in the context of biomass pyrolysis. In Jarihul's publication paper is mentioned among the biomass types. And paper contains 85%-99% of cellulose and 0%-15% of lignin. This composition is similar to the composition of fibre sludge. Therefore, it could be possible to suppose that the pyrolysis of fibre sludge with CO_2 might also produce syngas alongside with the biochar, as in case of the paper pyrolysis. And the biochar is reported to be effective adsorbent for such heavy metals as As(V) in acidic water. The adsorption capacity obtained during the study was 34.1 mg/g. The reason of this effectiveness is the catalytic effect of calcium and iron present in the paper mill sludge. (Cho, Kwon, Yoon, Tsang, Ok, Kwon & Song 2017.) Several literature sources have also confirmed the presence of Ca and Fe in fibre sludge. As mentioned earlier in Table 4 Fe and Ca are among the major elements in fibre sludge. These elements are obtained during the pulp and paper and wastewater treatment processes. (Cho, Kwon, Yoon, Tsang, Ok, Kwon & Song 2017; Nilsson 2009 [Svärd & Eskilsson 2001].) Under pyrolysis of the fibre sludge the iron and calcium turn into magnetite and calcium carbonate correspondingly. Thus, magnetic biochar is formed. The magnetite attracts metals. (Cho, Kwon, Yoon, Tsang, Ok, Kwon & Song 2017.) Based on Swärd's and Cho's research studies, it is possible to suppose that magnetite might also be present in fibre sludge pyrolized with CO_2. Therefore, the charcoal obtained via pyrolysis of fibre sludge with CO_2 might be effective for removal of such heavy metals as As(V).

3.2 Effect of chemical activation on the fibre sludge adsorption properties

A study has been conducted in Switzerland, where fibre sludge from Processum Ab, the Swedish pulp and paper mill, has been used. The cellulose and hemicellulose content in this fibre sludge was 95% and 4,75% correspondingly. The sludge had quite small content of negative charge, which means low affinity to metal cations. For this reason, the fibre sludge was subjected to chemical activation. Prior to the activation the cellulose nano fibers (CNF) were grinded into a 2wt% aqueous dispersion until the gel formation. The sludge was been modified by oxidation reaction using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2831.) The TEMPO oxidised cellulose nano fibers (TOCNF) have been prepared as follows. The CNFs were mechanically beaten and after that dispersed in water solution of NaBr and TEMPO. Then sodium hypochlorite was added dropwise into the obtained mixture. At the same time the pH of the reaction was being kept at level 10 by means of NaOH addition. Four different amounts of hypochlorite added resulted

in formation of four oxidation degrees. The oxidized sludge was then washed in deionized water. After that it was dispersed in water and disintegrated to prepare a TOCNF water suspension. (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2833.) Thus, carboxylates were introduced to the surface of fibre sludge. Negatively charged calboxylate entities can interact with positively charged particles, namely metals. The interaction occurs by means of electrostatic attraction. The metals used in the adsorption study include, Cu, Co, Ni , Cr, Zn. (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2831.) The adsorption experiments were conducted by adding the modified fibre sludge particles into solutions of the metal sulphates. For the sake of comparison similar adsorption experiments were also conducted with Montmorillonite nano clay, the commercial adsorbent. (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2834-2835.) The experiment results are summarised in Table 9 below.

TABLE 9. Properties of fibre sludge-based adsorbents. (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2834-2835)

Notation	**Preparation method**	**COOH groups (mmol/g)**	**Oxidation degree**	**Specific surface area (m^2/g)**	**Diameter (nm)**
CNF	Mechanical disintegration	0.10	0.01	229	11.6
TOCNF.04	TEMPO oxidation	0.26	0.04	330	8.1
TOCNF.14	TEMPO oxidation	0.86	0.14	267	10
TOCNF.21	TEMPO oxidation	1.21	0.21	303	8.8
TOCNF.26	TEMPO oxidation	1.50	0.26	345	7.8

The data in the table shows the increase of oxidation degree along with the amount of carboxylate groups. The general positive effect of TEMPO to the specific surface area and particle size of the adsorbent is also visible. The more the oxidation, the smaller the particles, and the bigger the surface area. The increased surface area speeds up the kinetics of the adsorption (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2839). The maximum adsorption value reached was reported to be 135 mg/g. The increase in metal adsorption after the chemical activation varies along with the pH and the negative charge content of the fibre sludge adsorbent. (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2831). This is well demonstrated in Figure 4.

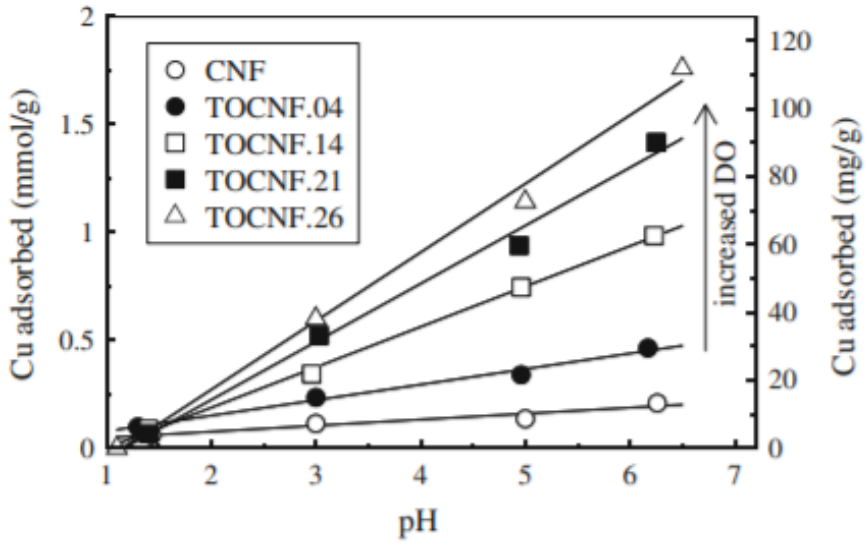

FIGURE 4. Copper adsorption to the original and modified fibre sludge. (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2837)

The graph shows significant improvement of adsorption after the TEMPO oxidation (FIGURE 4). The adsorption dependence on the pH is also interesting to trace. The adsorption is best at high pH. Whereas, almost no metal is adsorbed at acidic pH, which is understandable. In the acidic pH the carboxylate groups are protonated and form carboxylic acid. As the pH increases, the protons leave the carboxylic acid, whose negative charge is then available for the metals. And the more carboxylic groups there are, the more metals are adsorbed. In other words, the higher the oxidation degree is, the better the adsorption is. As the figure states, the highest adsorption occurred at the pH of 6.2 and at the oxidation degree of 26. (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2837).

The kinetic study of the TOCNF.26 revealed that 93% of the metals were adsorbed within 10 s. However, almost no further adsorption was noticed after 100 s. An interesting experiment was conducted in order to determine the competitive advantage of the biobased adsorbent over the commercial alternatives. Montmorillonite, the inexpensive commercial adsorbent was tested in similar experimental conditions as the fibre sludge. The comparison of the results showed that the fibre sludge adsorbent removed 2.4 times more copper from the water than the Montmorillonite. Moreover, the TOCNF adsorbents were recognised to work better than the other bio-based adsorbents. Therefore, TOCNF adsorbent has a potential to replace its existing competitors on the market in the future. (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2840). In addition to all the mentioned advantages of TOCNF adsorbent it has one more strength. Due to low metal affinity to the oxidized fibre sludge at low pH, it

is possible to recycle the adsorbent in acidic water. This was proven experimentally. (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2840). The results are presented in Figure 5.

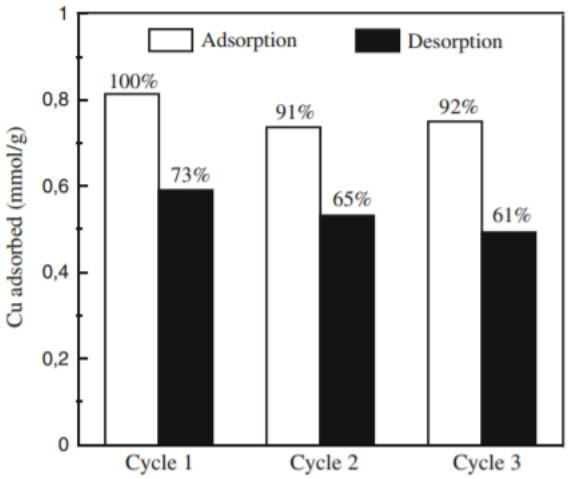

FIGURE 5. Recycling experiments of TOCNF adsorbent. (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2841)

The adsorption-desorption experiments were conducted in 3 cycles (FIGURE 5). In the first cycle 73% of the adsorbed copper metal ions were desorbed. In the second and third cycle 65% and 61% of the adsorbed material was desorbed respectively. It is also noticeable, that more than 90% adsorption was achieved in all three cycles. (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2840). The study also showed the ability of TOCNF.26 to adsorb Cr, Ni and Zn beside Cu. However, the metals were not combined in the same mixture during the experiments. The selectivity study has not been performed. (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2842). Therefore, no solid conclusions can be made about the success of TOCNF.26 adsorbent in real wastewater and in industrial scale. Another limitation of this research should also be mentioned. The impact of specific surface area of the fibers to the adsorption efficiency was not studied in this research (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2838).

3.3 Fiber sludge adsorbs metals without any pretreatment

In 2012 a group of researchers proved that fibre sludge removes heavy metals from water without any pretreatment (Suryan & Ahluwalia 2012, 1333). The adsorbent was prepared in the following way. The fibre sludge was collected from the filter bed of the effluent treatment plant. It was the Shri Gopal unit

of the Ballarpur industries Limited, Yamunanagar (Haryana). The sludge then was washed in distilled water, oven dried, powdered and stored in a polythene bag. In a separate interview Alhuwalia, one of the researchers mentioned that the sludge was activated before the adsorption experiment. Activation can be executed via heating or adding some chemical (Lassi 2020). No chemical addition was reported in the article. Therefore, it is possible to assume that the sludge was activated during the drying step.

The researchers studied how different parameters affect adsorption. Among them were pH, concentration of biomass, contact time and initial concentrations of metal ions. (Suryan & Ahluwalia 2012, 1332-1333.) Equilibrium was also studied. The study was conducted as follows. The solutions of nickel, cadmium, lead and copper were prepared from metal salts. The pH of the solutions was adjusted to 4.5. Each solution was mixed with the biomass and agitated. The equilibrium was reached within 10 h. The equilibrium of the adsorption was characterized by Langmuir and Freundlich models (Suryan & Ahluwalia 2012, 1333.) The constants and correlation coefficients of both models are given in Table 10. (Suryan & Ahluwalia 2012, 1337.)

TABLE 10. Values of Langmuir and Freundlich adsorption constants evaluated from isotherms and correlation coefficients (R2) (Suryan & Ahluwalia 2012,1337)

Metal	**Equilibrium Constants**					
	Langmuir Model			Freundlich Model		
	K	B	R^2	N	K_f	R^2
Pb	1.0768	7.3736	0.8905	1.57	3.17	0.97
Ni	7.8612	2.5625	0.8566	1.95	2.42	0.96
Cd	1.8602	4.3449	0.7702	2.44	4.47	0.93
Cu	3.6309	5.3575	0.9814	1.71	4.09	0.98

As the table shows, all the four metals, which are lead, nickel, cadmium and copper, fitted both models quite well. This conclusion can be drawn because the correlation coefficient R^2 values are very near to one in all cases. The Cd, however, rather fits the Freundlich model than the Langmuir. These results mean that the adsorbent attracts all four metals almost equally well. (Suryan & Ahluwalia 2012, 1337.) It is noticeable that 70% of metals were adsorbed within 15 min. And all the metals adsorbed well within a wide pH range. During this study the effect of different parameters on the adsorption efficiency was investigated. Among the parameters are pH, contact time, initial metal concentrations in water, biomass concentration, surface area, temperature and pressure. The obtained results and conclusions are presented in Chapter 4.

3.4 Principles of bonding between metals and the adsorbent

According to literature there exist two types of adsorption. They are physical and chemical. Physical adsorption is a process where the Van Der Waals forces hold an adsorbate to an adsorbent. These forces do not vary among chemical nature of the materials. Physical adsorption increases with the pressure and decreases with the temperature. Chemical adsorption, in its turn, involves chemical bonds that are specific for each adsorbent and adsorbate. This type of adsorption works at higher temperatures than physical adsorption. (Britannica 2020.) Fibre sludge contains organic and inorganic components (Nilsson 2009). Therefore, its mechanism of adsorption involves both an ion exchange and a physico-chemical adsorption. (Suryan & Ahluwalia 2012, 1336.) Even though ion exchange is a different process than adsorption, it can occur, if an adsorbent obtained certain functional groups via chemical activation (Lassi 2020). Concerning the three adsorbent cases described in Chapters 3.1, 3.2 and 3.3, it was difficult to understand the processes during the adsorption. No metal adsorption experiments with pyrolyzed fibre sludge were found in literature. The adsorption process in the study of the non-modified fibre sludge was also not described, as the focus in that study was kept on the adsorption results rather than the process. The adsorption mechanism is clear only in the experiment with the TEMPO-activated sludge. The process there is chemical adsorption. The carboxylate-ends of the activated sludge chemically bonded with the metals in water, as described in Chapter 3.2.

4 PARAMETERS AFFECTING ADSORPTION

This chapter focuses on impact of various parameters on the adsorption capacity and adsorption speed of the fiber sludge. The parameters include pH, contact time, initial metal concentrations in water, biomass concentration, surface area, temperature and pressure. The impact of pH was investigated experimentally. Adsorption experiments were conducted at different pH levels. After the adsorption the amount of residual metal was measured. Similar experiments were conducted by researchers to determine the effect of fibre sludge concentration on adsorption. The influence of contact time and initial metal concentration on adsorption were also tested. These results were found reported in literature and are presented in this chapter. No data about the impact of other parameters mentioned was found in literature. Therefore, some information on this issue was obtained via interviews with researchers.

4.1 Effect of pH

According to Devi & Sahora the key role in adsorption belongs to pH, due to surface chemistry. The pH level affects ionization capacity of the adsorbate, surface charge and functional groups of the adsorbent. It was found that metal adsorption improves from acidic to neutral pH. In this range hydrogen ions are easier substituted by metal ions. In basic pH a hydrolysis of metals occurs, which significantly complicates the adsorption. (Devi & Saroha 2016, 26.) Suryan and Alhuwalia have worked in an acidic to neutral pH range, namely 2 to 5. The results are shown in Figure 6 below. The graph represents the dependence of residual metal concentration on the pH level. The optimal pH level for all the metals is visible as the lowest line (FIGURE 6).

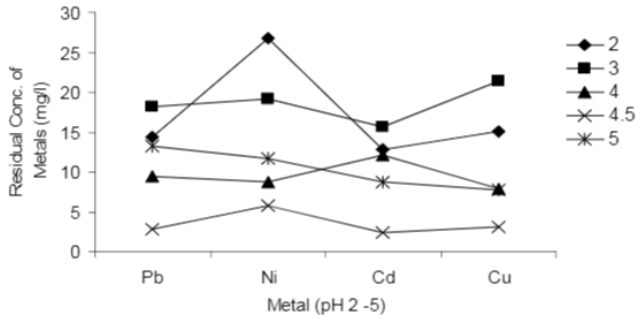

FIGURE 6. Effect of pH on the %removal of different metals by paper mill waste (Dry biomass: 1.0%, Temp.28±20C; Agitation 100 rpm for 1 hr, Initial conc. (Ci) 50 mg l-1) (Suryan & Ahluwalia 2012, 1334)

The pH of lowest residual concentration and of the highest adsorption for all the metals is 4.5 (FIGURE 6). However, concerning this graph the following peculiarities can also be noticed. The worst metal to adsorb at pH of 2 is nickel. This metal adsorbed best at pH of 4 and 4.5. The least amount of lead, cadmium and copper was adsorbed at pH of 3. Lead adsorbed better at pH of 4 than at pH of 5. This means that the dependence of the adsorption efficiency on the pH level is not linear. Despite these details, according to Suryan and Alhuwalia the pH level within the studied range was not significant (Suryan & Ahluwalia 2012, 1338). The results showed that the adsorption was above 70% for all the metals within the pH range from 2 to 5 (Suryan & Ahluwalia 2012, 1338).

4.2 Effect of fibre sludge concentration

In the same study by Suryan and Alhuwalia the effect of biomass concentration on the adsorption efficiency was investigated. A series of batch experiments was conducted with the biomass concentrations of 0.5%, 1%, 1.5% and 2.0%. The tests were performed for each metal. The stock solutions were prepared for each metal separately. The metals were not mixed into the same solution in Alhuwalia's study. The experiments were conducted at the pH of 4.5. This pH level was found to be optimal for mrtal adsorption in previous experiments. And the metal concentration in water was near 50 mgl^{-1}. (Suryan & Ahluwalia 2012, 1333.) The results can be seen in Figure 7 below. The graph represents the dependence of residual metal concentration on the concentration of fibre sludge or biomass.

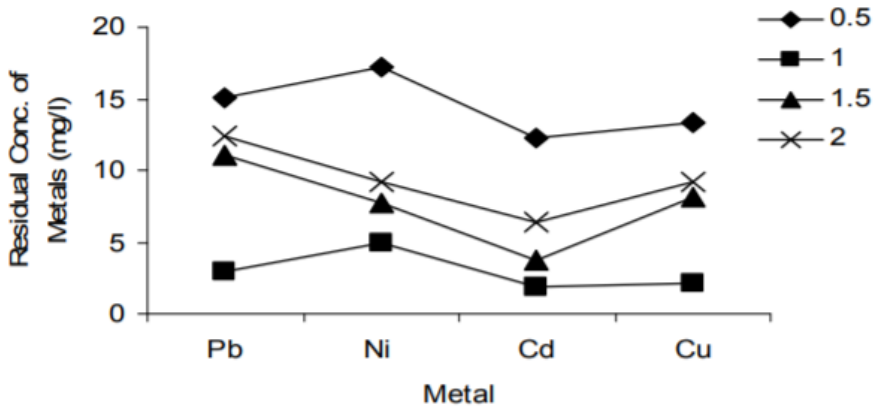

FIGURE 7. Effect of Biomass concentration (w/v) on the %removal of different metals by paper mill waste (Temp.28±20C; pH. 4.5, Agitation 100 rpm for 1 hr, Initial conc. (Ci) 50 mgl^{-1}. (Suryan & Ahluwalia 2012, 1334)

All metals behaved similarly over the concentration range. It is noticeable that the adsorption dependence on concentration is not linear. As the figure shows, the lowest adsorption occurred at the biomass concentration of 0.5%. And the highest adsorption was at fibre sludge concentration of 1% (FIGURE 7). Less metal was adsorbed at the biomass concentrations of 1.5% and 2% than at the concentration of 1%. Interestingly, the adsorption efficiency at fibre sludge biomass concentrations of 1.5% and 2% was higher than it was at the concentration of 0.5%. (Suryan & Ahluwalia 2012, 1334.) But even though the dependence is not linear, the trend is same for cadmium, copper, nickel and lead. The adsorption of all the metals improves at biomass concentrations in the following order 0.5%, 2%, 1.5%, 1%.

4.3 Effect of contact time and initial metal concentration in water

The contact time and initial concentration of metals in water were investigated. They also had some effect on adsorption. The residual concentration over the time of agitation was studied. The metals used in the laboratory experiments were Cd, Cu, Pb, an Ni. Solutions of each metal were prepared separately. The pH was 4.5. The initial concentration varied from 5 to 100 mgl^{-1}. The concentration of the adsorbing biomass was 1%. The samples were agitated for 5 hours at 100 rpm. The samples were taken at different time intervals. Then their residual metal concentration was determined. (Suryan & Ahluwalia 2012, 1334.) The impact of initial metal concentration and agitation time on the residual metal concentration is presented in Figure 8.

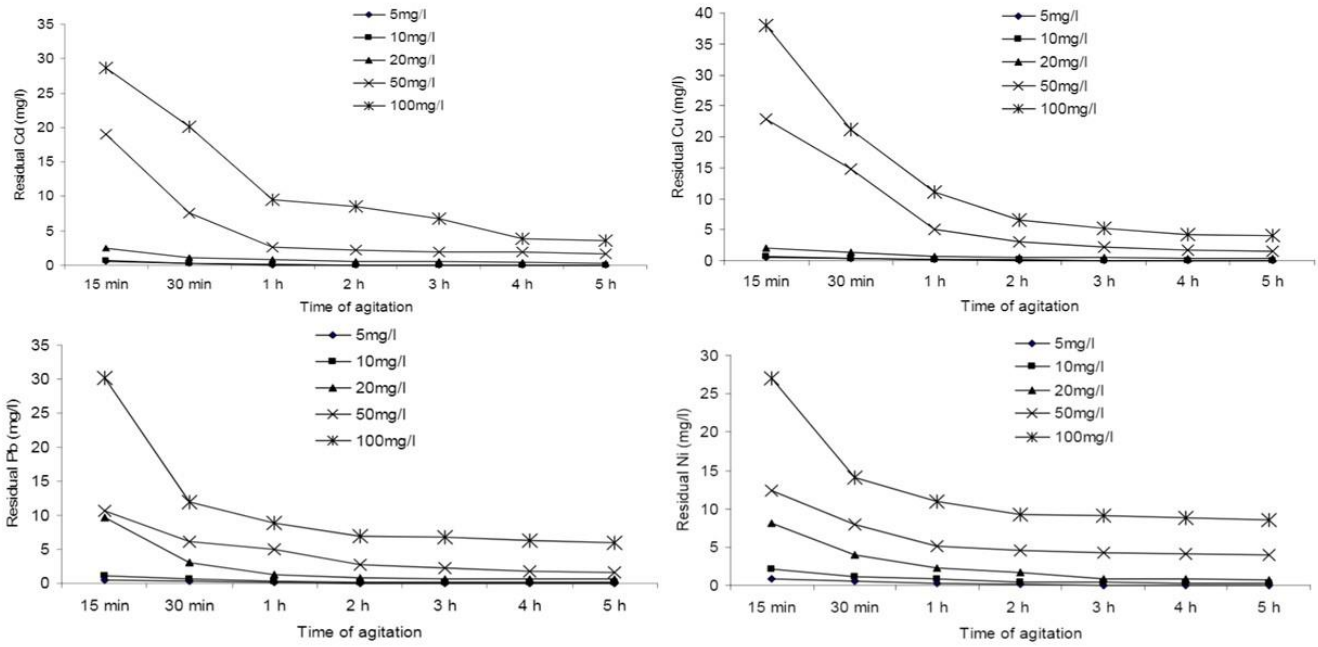

FIGURE 8. Effect of initial concentration (Ci) of Cd, Cu, Pb, and Ni with time of agitation on residual concentration. (Temp.28±20C; pH. 4.5, Agitation 100 rpm, Biomass conc. 1% w/v) (adapted from Suryan & Ahluwalia 2012, 1335)

According to Figure 8 most of the Cd metal is adsorbed during the second 15 min in all cases of initial metal concentration. And after 4 hours the residual concentration in each case is below 5 mg/l. Concerning Cu, most of the metal is adsorbed during 1 hour in all cases. And as in the experiment with Cd the residual concentration in each case is below 5 mg/l after 4 hours. The initial Pb concentration in water has the same effect of adsorption as in the case with Cd. Most of the metal is adsorbed within the first 30 min regardless the initial concentration. Similar trend is observed in the experiment with Ni. The metal is almost completely removed after 30 min. And after several hours the residual concentration does not exceed 15 mg/l. The overall conclusion for all the four metals studied is as follows. It was found that 70%-89% of metal ions were adsorbed from initial metal concentration of 100 mgl^{-1} and 5 mgl^{-1} correspondingly within 15 min of time. (Suryan & Ahluwalia 2012, 1335.) There was a decrease in adsorption in first 15 min for Cd and Cu at 50 mg l^{-1} and for Pb and Ni at 20 mgl^{-1}. However, the adsorption increased with increase of contact time. At equilibrium 99.8 % Ni, 98.0% of Pb, 99.2% of Cu, 99.8% of Cd was adsorbed at initial metal concentration of $5mgl^{-1}$. At the remaining concentration range, the adsorption decreased but kept the level above 90%. (Suryan & Ahluwalia 2012, 1335.) In the context of Suryan's and Alhuwalia's research, the initial metal concentration might not be significant. However, its significance in industial conditions depends on how critical the adsorption time and the

residual concentration would be for the industrial process. The contact time would not be a significant parameter in the context of the laboratory research, if 70%-89% were sufficient values for the adsorbed metals. At these values all four metals adsorb within 15 min in initial metal concentrations from 5 mgl^{-1} to 100 mgl^{-1}. (Suryan & Ahluwalia 2012, 1335.) If the targeted adsorption is near 100%, then lower initial metal concentrations, e.g. 5 mgl^{-1} will need only 15 min to remove the metals. Whereas higher concentrations e.g 100 mgl^{-1} will require longer contact time, 2-5 hours depending on the metal to be adsorbed. (Suryan & Ahluwalia 2012, 1335-1336.)

4.4 Effect of surface area

Other parameters affecting adsorption include surface area. According to Alhiwalia surface area is the key parameter. The smaller the adsorbent particle, the better the adsorption. Some people even pulverize their samples to enhance adsorption. (Alhuwalia 2020.) This conclusion is valid for the laboratory scale. Whereas, in the industrial scale process design sets some limitations. If the adsorbent particles are too small or if the adsorbent granules disintegrate under the water flow, they might flow out along with the water. In this case a filtration unit would be necessary to add in order to remove the adsorbent particles from the water. An extra unit would demand an extra investment. This issue was mentioned earlier in Chapter 2.

4.5 Effect of temperature and pressure

Several physicochemical parameters influence adsorption. One of the goals of this thesis was to understand how such process conditions as temperature and pressure would affect the metal adsorption from water in industrial scale. An e-mail interview of Sarabjeet Alhuwalia, the researcher, was conducted for that purpose. According to the discussion, temperature has insignificant impact to the adsorption. And most adsorption experiments were performed at ambient temperatures in his study. The impact of pressure to the adsorption was not studied in Alhuwalia's research work. (Alhuwalia 2020.) Neither was it mentioned in other literature sources used in this study. Therefore, the impact of pressure for the adsorption remains unknown.

4.6 Effect of functional groups

The properties of adsorbent depend on the functional groups on its surface (Jaria, Silva, Ferreira, Otero & Calisto 2016, 209). According to Alhuwalia, functional groups to be formed on the surface of fibre sludge depend on several factors. They include the type of metal to be adsorbed, the raw material used in paper industries and the specifications of the pulping process. (Alhuwalia 2020.) A similar point of view is also expressed in Jaria's and Silva's research. According to their findings, fibre sludge from different factories might have different properties. This issue originates from chemical content variability between samples of different factories. Therefore, it is not recommended to mix fibre sludge feedstocks obtained from different factories into one batch. (Jaria, Silva, Ferreira, Otero & Calisto 2016, 209.)

5 CONCLUSION

The aim of the thesis was to detect if fibre sludge can work as an adsorbent for metals and is it effective without any modifications. According to literature, fibre sludge was proved to be a green, abandoned and recyclable adsorbent material (Sehaqui, Larraya, Liu, Pfeninger, Mathew, Zimmermann & Tingaut 2014, 2842). According to Jaria's research fibre sludge is a homogeneous and consistent material. That means that fibre sludge samples from the same factory have the same properties. It was also found that fibre sludge- based adsorbent has low mechanical strength. The granules do not withstand the adsorption. However, this conclusion was made for the pyrolyzed fibre sludge. In Alhuwalia's and Sehaqui's researches mechanical strength of the adsorbents was sufficient. Based on the studies conducted by Suryan and Alhuwalia, fibre sludge was concluded to be an effective adsorbent for removal of Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+} from aqueous solutions. Among the four metals, all were adsorbed equally well at equilibrium. Their adsorption efficiency varied from 98% to 99.8%. The metals adsorbed at equilibrium are listed in a descending order as follows: Ni^{2+} and Cd^{2+}, Cu^{2+}, Pb^{2+}. (Suryan & Ahluwalia 2012, 1335.)

During this literature review the key parameters affecting adsorption were studied. Among them were surface area of the adsorbent, pH range, contact time and initial metal concentration in water. According to Alhuwalia's research, the best pH for the metal adsorption was 4.5. The best biomass concentration was 1%. According to Alhuwalia's research the initial metal concentration in wastewater had small effect on adsorption. However, the effect of metal content in the ash of fibre sludge has not been studied, but it would be interesting to know. Concerning the process conditions of adsorption, temperature was found insignificant. And the impact of pressure was not researched. No selectivity study was conducted in Alhuwalia's research. And the metal solutions used were prepared in the laboratory. The experiments were performed using stock solutions of each metal. Moreover, no other cases of non-modified fibre sludge adsorbing metals were found in literature. Therefore, Alhuwalia's conclusions are specific. And the behavior of the adsorbent in a real industrial wastewater with a mixture of different metals and other substances is unknown.

The effects of pre-treatment methods on the fibre sludge adsorbent were also evaluated. The pre-treatment methods studied were pyrolysis and chemical activation. The charcoal yield of the pyrolysis varies from 4% to 58 % among different researches. The advantages of pyrolysis were formation of magnetite and possibility to produce syngas. The syngas could be used or used as energy. And magnetite improves the adsorption properties of fibre sludge towards metals. However, it might not form, if ash is completely

removed prior to pyrolysis. The advantages of the chemical activation, the TEMPO-activation, of fibre sludge were as follows. The adsorption process completed much faster than in case of non-modified fibre sludge. Above 90% adsorption yield was achieved within 10 s. The metals adsorbed were Cu, Cr, Ni and Zn. The best pH in this study was 6.2. In acidic pH protonation of functional groups occurs, which makes it difficult for metals to adsorb. Thus, it is possible to recycle the adsorbent in acidic pH. Nearly 70% of metals were experimentally desorbed from fibre sludge in low pH. It is noticeable that TEMPO-activated fibre sludge adsorbent removes 2.4 times more metals from water than the commercial adsorbent. Despite all the mentioned advantages, there are limitations. No selectivity study was conducted in that experiment. The experiments were carried out using stock solutions of each metal. Therefore, there is no guaranty that the fibre sludge adsorbent will be as effective in the industrial scale application.

Considering the results reported in literature used in this thesis, the following conclusion can be made. Adsorption is affected by the pH, contact time, initial metal concentrations in water, biomass concentration, surface area. The degree of impact of these parameters is defined by the functional groups of the fibre sludge. For instance, the TEMPO-activated sludge had different functional groups than the non-modified sludge. Therefore, the sludge adsorbed metals in different pH levels. The functional groups of the original fibre sludge depend on the pulping process technology and the raw material used. Fibre sludge feedstocks of various origins might differ in their adsorptive properties. Therefore, it is not recommended to use feedstocks from different factories for the adsorbent production. The laboratory studies described in the thesis report fibre sludge to be a suitable and even commercially competitive material for metal adsorption from water. Therefore, industrial scale experiments using real wastewater are to be conducted to prove the reliability of fibre sludge to be an adsorbent or its precursor.

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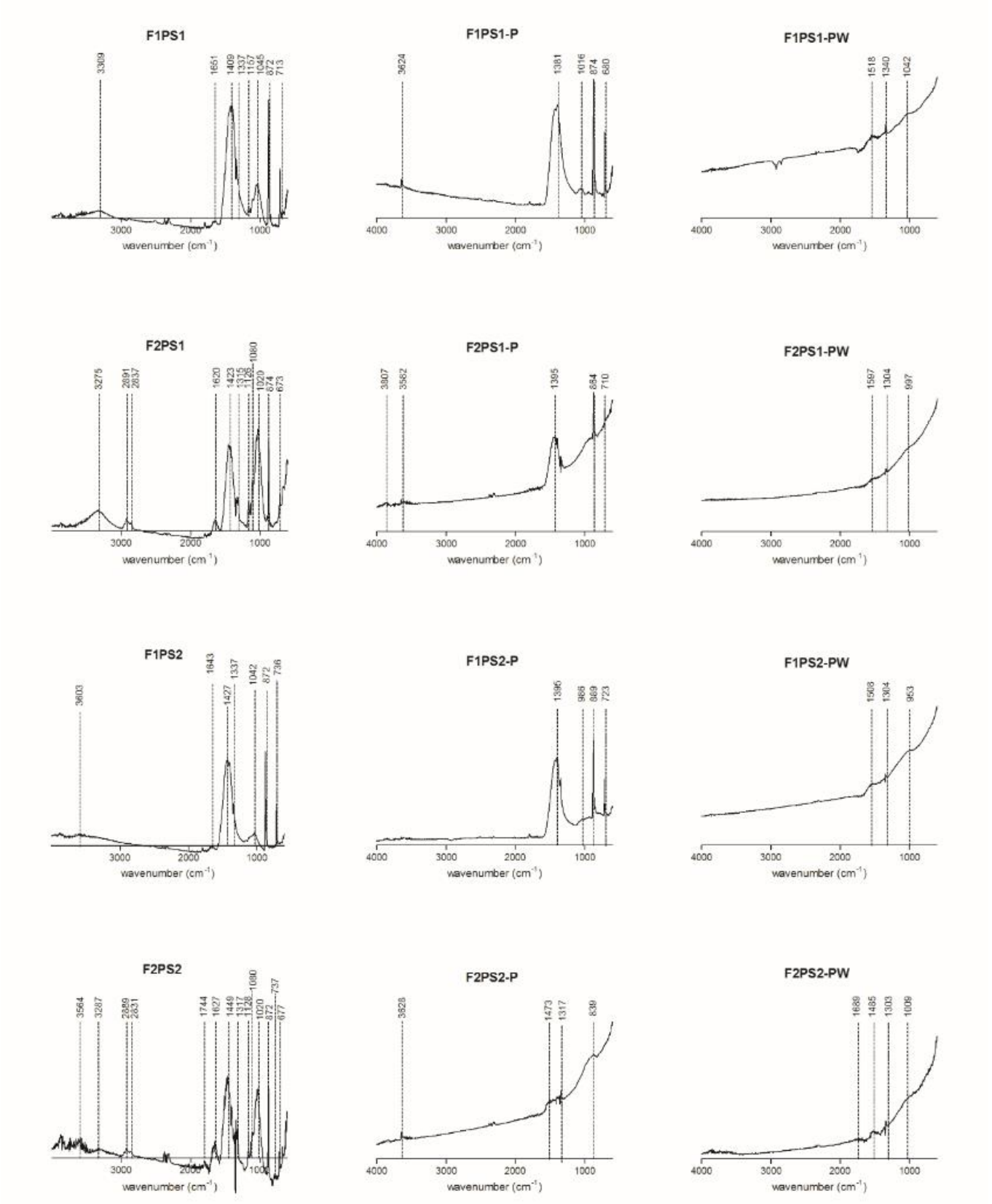
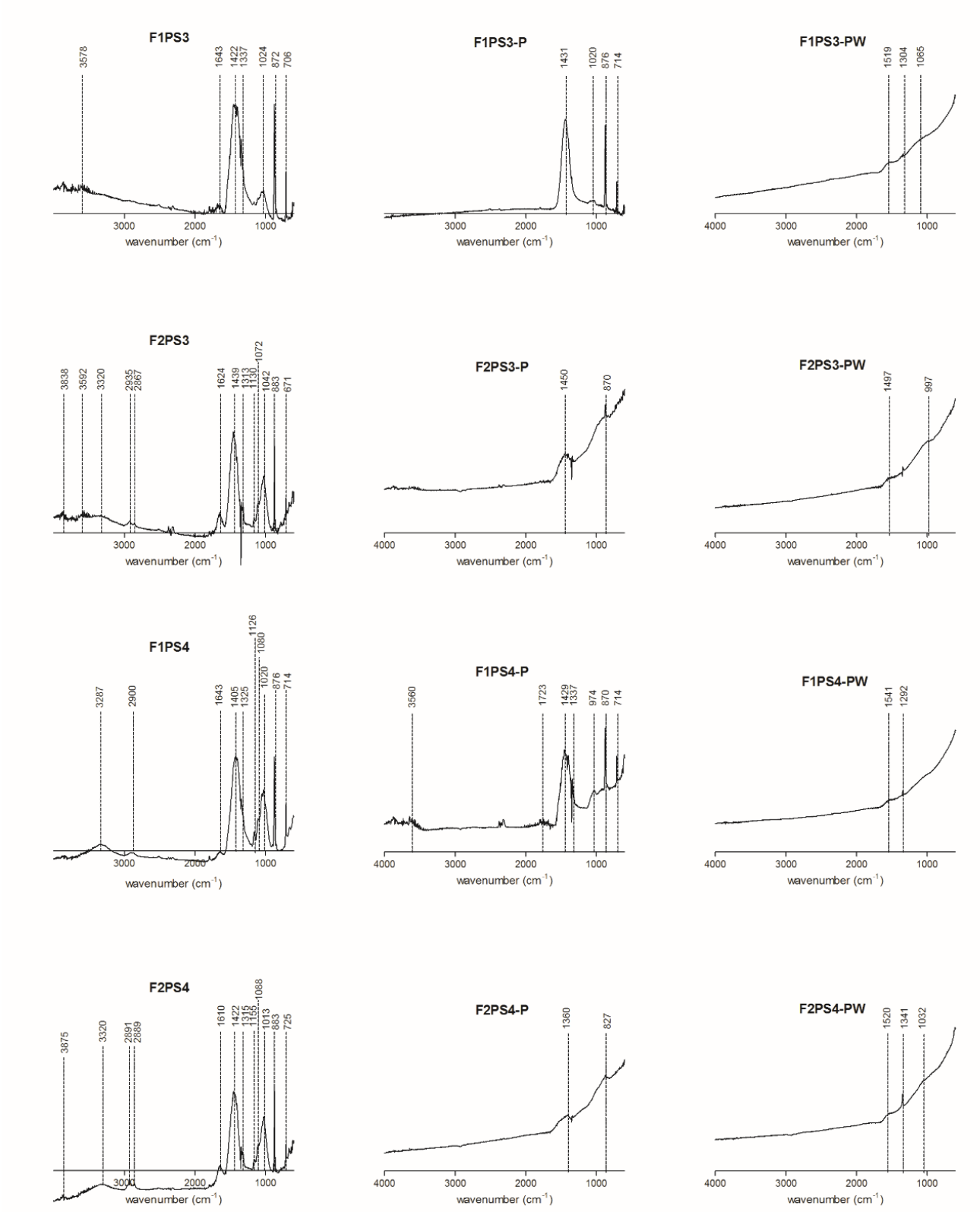


ATR-FTIR spectra of PS raw materials and carbon adsorbents (P and PW materials) produced from them (samples 1 and 2). (Jaria, Silva, Ferreira, Otero & Calisto 2016 [supplementary data, S3])



ATR-FTIR spectra of PS raw materials and carbon adsorbents (P and PW materials) produced from them (samples 3 and 4). (Jaria, Silva, Ferreira, Otero & Calisto 2016 [supplementary data, S3])