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Tailored mesoporous biochar sorbents from pinecone biomass for the adsorption of natural organic matter from lake water

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(Article begins on next page)

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| 2 | organic matter from lake water |
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31 Abstract

32 Natural organic matter (NOM) raises major issues for drinking water treatment including undesirable taste 33 and color, formation of carcinogenic disinfection by-products (DBPs), and promotion of microbial regrowth 34 in the water distribution system. As such, mesoporous biochars have been tailored from pine-forestry byproducts for treating NOM and color causing compounds from drinking water sources, such as lakes. Herein, 35 36 several tailored biochars are fabricated via two procedures: pre-pyrolysis/activation/post-pyrolysis and 37 activation/post-pyrolysis processes, using NaOH and ZnCl₂ activators to improve the surface chemistry and 38 porous structure for higher NOM adsorption. The mesoporous biochars, pristine biochars, and pinecone 39 biomass are characterized via several characterization analyses including Brunauer, Emmett and Teller 40 surface area measurement (BET), thermogravimetric analysis (TGA), and scanning electron microscopy 41 (SEM). Batch experiments are conducted to study the adsorption isotherm, kinetics and mechanism along 42 with desorption. Characterization revealed effective characteristics of tailored biochars for NOM adsorption 43 including mesoporous structure, remarkable surface area (up to 1470 m²/g), high thermal stability, and 44 elevated carbon content. All the tailored biochars showed improved removal capacities for NOM and color 45 compounds from real lake water samples compared with those of the pinecone biomass and pristine 46 biochars. The most promising tailored biochar (herein named as TB-N-I) was developed by NaOH modification 47 via pre- and post-pyrolysis processes. With the lowest optimized dosage (0.25 g/L), TB-N-I removed more 48 than 80 % of both NOM and color from the lake water (COD: 13.4 and color: 53.65 mg/L), superior to the 49 removal capacity of commercial powdered activated carbon (PAC). Acidic conditions significantly favored the adsorption, e.g., NOM removal by TB-N-I from the lake water reached 97 % at pH 2. Nonlinear regression 50 51 provided a good fit for Freundlich and Sips (r^2 = 0.988 and Δq = 0.08) isotherms as well as pseudo-second-order 52 kinetic models. This suggests the heterogeneous distribution of the adsorptive sites at the biochar surface 53 and the multilayer nature of NOM adsorption. A desorption study revealed that more alkaline solutions 54 resulted in higher NOM desorption (30 mM NaOH > 3 mM NaOH > distilled water), yielding regenerated adsorbents with high re-adsorption capacity. Liquid chromatograph-organic carbon detection (LC-OCD) was 55 56 used to study the removal of different NOM size fractions, e.g., low molar mass (LMM) fraction of NOM, 57 which are more hydrophilic and resistant to conventional treatments. Of significant interest, LC-OCD 58 indicated that TB-N-I removed 20% more of the problematic LMM compared with that of PAC. Effective pore 59 size distribution of tailored biochar (TB-N-I) for the adsorption of NOM fractions was indicated by BET analysis 60 and was confirmed by LC-OCD.

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Keywords: Biochars; Modification; Mesoporosity; Adsorption; Natural organic matter; Removal mechanism
 63

64 1. Introduction

66 Biochars are being utilized for a wide range of applications, including environmental management such as remediation of soil, management of waste, and mitigation of climate change [1-3]. Thermal treatment of 67 68 biomass via pyrolysis in a limited oxygen atmosphere results in biochar, bio-oil, and syngas [3, 4]. Biochar 69 production from waste biomass is both economical and environmentally beneficial [1]. Owing to their porous 70 structure, relatively high surface area, and enriched surface chemistry, there is a growing interest for biochars 71 as sustainable media in engineering value-added materials [2]. They can be produced near the point of 72 application and/or near biomass sources in both small-scale pyrolysis units and in large-scale integrated 73 refinery facilities that are designed for simultaneous biochar and energy production.

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75 The biomass composition and production conditions can influence the yield and properties of the biochars 76 [5]. Biochars are typically developed from abundant biomass sources such as wood. Low-temperature 77 pyrolysis (400-500 °C) yields enriched porous biochars with low oxygen and hydrogen content [4]. Biochars 78 developed at higher temperatures (>700 °C) provide elevated aromaticity, hydrophobicity, surface area, 79 mesopores and micropores. These properties make them a high quality and eco-friendly alternative to, for 80 instance, coal-based activated carbons for water purification [6]. Surface properties of biochars can be also 81 manipulated through activation/modification [7]. Chemical activation uses chemicals to oxidize the surface 82 and generate desired functional groups [7]. Enhanced oxygen-containing surface functional groups enable 83 the possibility of specific binding (e.g., hydrogen bonding and π - π electron-donor-acceptor interactions) [8]. 84 The hydrophobic surface of biochars results in adsorption affinity for hydrophobic organic compounds, 85 including pharmaceuticals and natural organic matter (NOM) [4, 6].

87 Agricultural and forestry by-products such as pinecones can be tailored into value-added materials, such as 88 biochars, providing adsorptive properties for contamination remedies [5, 6, 8-15]. The pine family comprise 89 economically important species in agriculture and forestry industries worldwide, especially in the Nordic 90 countries. These species produce large quantities of pinecones as by-products annually. Pinecones are 91 composed of imbricated woody scales, containing cellulose, hemicelluloses, and lignin. Availability and high 92 lignocellulosic content make pinecone a suitable and cost-effective biomass for biochar production. 93 Unmodified biochars however exhibit limited adsorption for anionic species [12]. The biochars can be further 94 modified through chemical or physical processes to increase their adsorptive properties according to the 95 target pollutant, the environmental condition, and the treatment goals [16]. Herein, we aim to tailor 96 mesoporous biochars through chemical modification for the adsorption of NOM from lake water. Tailoring 97 through chemical modification, e.g., alkali activation, can enhance the surface functionality and structure of 98 biochars [7] for higher adsorption of our target pollutant, NOM, from lake water.

100 NOM in natural water sources negatively affects the drinking water treatment and the finished water quality. 101 For instance, it causes taste and color problems, raises the coagulant and oxidant/disinfectant demand, acts 102 as a precursor to disinfection by-products (DBPs), and promotes microbial regrowth in water distribution 103 system [17, 18]. NOM is treated conventionally by chemical coagulation, or by adsorption onto activated 104 carbon (AC) [19]. The adsorption depends on the characteristics of the NOM, the adsorbent and the water. 105 For instance, molecular mass size and hydrophobicity of NOM control its adsorption. NOM consists of high 106 molar mass (HMM) fraction such as humic compounds, easily removable by coagulation, and intermediate 107 molar mass (IMM) compounds, more controllable by adsorption [17, 19]. However, of significant concern is 108 the low molar mass (LMM) fraction of NOM such as tannic acids, which are more hydrophilic and resistant to 109 common treatments. As NOM adsorption primarily takes place by pore filling mechanism, it is largely 110 influenced by the relationship between the pore size distribution of the adsorbent and molecular size of NOM 111 [17]. Mesopores (2-50 nm width) accompanied with sufficient amount of micropores (< 1 nm in width) can 112 therefore provide high adsorption capacities for different fractions of NOM e.g. LMM [17, 19].

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114 Our objective is to tailor biochars with high content of mesopores accompanied with microspores and desired 115 surface functional groups though chemical modification towards higher adsorption of NOM, especially the 116 problematic LMM fraction, from lake water. The adsorbents are fabricated via two pathways involving one-117 step pyrolysis or two-step pyrolysis. Sodium hydroxide, NaOH, and zinc chloride, ZnCl₂, are used to modify 118 the interfacial and structural properties of the pinecone-derived biochar for higher adsorption of NOM. 119 However, adsorption studies are mainly performed under single-solute condition (synthetically made organic 120 matter solutions) and are not evaluated for the treatment of natural water, e.g. lake water. It is important to 121 scrutinize the removal performance of the developed adsorbents in representative water matrices as was 122 done in this study. To study their structure and composition, the adsorbents are characterized via characterization methods such as Brunauer, Emmett and Teller (BET) specific surface area/porosity, 123 124 thermogravimetric (TGA), and scanning electron microscopy (SEM). The tailored biochars are evaluated for 125 removing NOM and color causing compounds from lake water through adsorption equilibrium, kinetics, and 126 mechanism and are compared with a commercial coal-based powdered activated carbon (PAC). The 127 adsorption of different NOM fractions, such as humic substances and LMM acids, by mesoporous biochars 128 and PAC are also analyzed via liquid chromatograph-organic carbon detection (LC-OCD).

- 129 2. Methodology
- 130 2.1. Materials
- 131

Pinecone biomass was obtained from Otaniemi campus of Aalto University, Finland, between September and
 November. The cones were washed repeatedly with tap and reverse osmosis water to remove impurities,

dried at 80°C for 24 h and crushed. The dried biomass was ground in a blender (11 basic Analytical mill, IKA)
and sieved using 80-µm sieve (Retsch GmbH Germany). The powdered biomass was stored at room
temperature in the dark and used for tailoring biochars. NaOH and ZnCl₂ were purchased from Sigma Aldrich.
A commercial coal-based powdered activated carbon (PAC) (Merck) was used for comparison. Sulphuric acid,
potassium permanganate, potassium iodine, starch-indicator, and sodium thiosulfate (Sigma Aldrich) were
used for the determination of chemical oxygen demand calibration curve.

140 141 2.2.

Fabrication of mesoporous biochars

142 Four types of biochars were tailored via one-step and two-step pyrolysis involving chemical modification; see 143 the illustration of the fabrication pathways as Figure 1 in [20]. In the pre-pyrolysis/activation/post-pyrolysis 144 process (I), dried powdered biomass was first pyrolyzed at 300 °C for 15 min under nitrogen gas (1 L/min) in 145 a laboratory-scale batch tube furnace (NBD-O1200, Nobody Material Science and Technology CO., LTD, 146 China). The weight loss from the thermal treatment was measured; 66±1% yield was achieved. Secondly, the 147 biochars were modified with NaOH and ZnCl₂. Pristine biochars were mixed with chemical solutions (1/2 weight ratio of biochar/activator) for 2 h, dried overnight at 105 °C, and thirdly heated for 2 h under nitrogen 148 149 gas at 800 °C. In the activation/post-pyrolysis process (II), dried powdered biomass was first mixed with the 150 chemical solutions (1/2 weight ratio of biomass/ activator) for 30 min followed by heating in an oven at 105 151 °C for 24 h. After drying, it was pyrolyzed at 700 °C for 2 h under nitrogen gas (1 L/min). The products were 152 rinsed with 0.1 M HCl and reverse osmosis water until neutral pH was reached and dried at 105 °C for 24 h. 153 The dried biochars were finally ground, sieved using 80 µm sieve, and stored at room temperature in the 154 dark for characterization and adsorption. The samples are referred to as tailored biochar (TB)-activator 155 (NaOH: N or ZnCl₂: Z)-method (II or I) e.g., TB-N-I. For comparison, pristine biochars were also produced via 156 pyrolysis at 300 and 700 °C (referred as B-300 and B-700).

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2.3. Characterization of mesoporous biochars

Brunauer, Emmett and Teller (BET) specific surface area and porosity analysis was conducted using Tristar II Micromeritics, USA, via the adsorption-desorption cycle of N₂ gas at 77.350 K onto the external surface of

the materials. Scanning electron microscopy (SEM) was carried out on a ZEISS SIGMA VP (1.8-2.0 kV acceleration voltage) to explore the surface morphology. Energy dispersive X-ray (EDX) analysis was performed on a JEOL JSM-7500FA analytical field Emission scanning electron microscope (15 kV acceleration voltage, emission current of 10 μA). To study the thermal stability, we carried out thermogravimetric analyses (TGA) on TA instruments – TGA Q500 (USA) from 20 °C to 800 °C at a heating rate of 10 °C/min under N₂ gas environment. A Nicolet 380 FT-IR infrared spectrometer was used for Fourier transform infrared spectroscopy (FTIR).

168 2.4. Raw water samples

Lake water samples were collected from Lake Pitkäjärvi in Espoo, Finland. Table 1 compiles the quality
characteristic of the lake water.

172

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Table 1

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2.4.1. NOM and color measurement

The concentration of NOM was estimated via UV absorbance measurement at 254 nm wavelength, using a 175 UV-1201 Shimadzu-spectrophotometer. The samples were filtered before the measurement through 176 177 Sartorius Minisart 0.45 µm filters. The absorbance was converted to concentration using the COD_{Mn} 178 calibration curve, see Figure 2 in [20]. To measure COD_{Mn}, a known amount of potassium permanganate 179 (Na₂Sa₂O₃) was added to acidified lake water samples using 4 M sulfuric acid. The samples were boiled for 20 180 minutes, where the oxidizing matter in the samples reduces part of the permanganate. The unreduced 181 portion of permanganate was measured by iodometric titration method and the amount of used 182 permanganate was used to calculate COD_{Mn}. The color of water samples was measured according to the SFS-183 EN ISO 7887. Samples were filtered and the absorbance was measured at 410 nm wavelength.

184 2.4.2. Liquid chromatograph – organic carbon detection (LC-OCD) measurement

Liquid chromatograph–organic carbon detection (LC-OCD) quantifies the elution as a function of size and
 affinity of carbon from a Toyoperal HW 50 s column using a buffered carrier solution [21]. The method was

calibrated using Suwannee River humic and fulvic acid standards. UV254 absorbance and organic carbon
were measured online and allowed quantifying the elution of DOC over time. UV254 absorbance was
measured with a K200 detector by Knauer, organic carbon was measured by first decomposing it to carbon
dioxide (CO₂) in a Gräntzel-reactor and then measuring the CO₂ with Ultramat 6 infrared detector by Siemens.
FIFFIKUS software was used to separate the acquired chromatograph into different apparent size fractions,
viz. biopolymers (molecular weight (MW) > 20 kDa), humic substances (MW ~ 1000 Da), building blocks (MW
300-500 Da), low molecular weight acids (MW < 350 Da), and low molecular weight neutrals (MW < 350 Da).

195 2.5. Adsorption

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197 Known amount of the adsorbent in 50 mL volume of lake water were used for the adsorption batch 198 experiments on a shaker (150 rpm and room temperature). The experiments were carried out without pH 199 adjustment, except for those studies where indicated. After the desired contact time, the solutions were 200 filtrated through Sartorius Minisart 0.45µm filters for the final COD_{Mn} concentration measurement. The 201 adsorbent dosage was optimized within 0.1–1 g/L range. The effect of pH was investigated through adjusting 202 the solution pH at values 2, 4, 8, and 10 using HCl and NaOH. The kinetics were explored at varying time 203 intervals between 1 min to 24 h. The batch experiments were conducted in two or three replicates. We 204 employed the following equations to determine the removal percentage and adsorption capacity:

205 Removal % =
$$\frac{(C_i - C_t)}{C_i} \times 100$$
 (1)
206
207 $q_t (mg/g) = \frac{C_i - C_t}{m} \times V$ (2)

where C_i and C_t (mg/L) are the initial COD_{Mn} concentration and the concentration at time t, respectively, V (L) is solution volume, and m (g) is adsorbent mass.

211 2.6. Desorption and re-adsorption

For desorption and re-absorption batches, 0.25 g/L dosage of TB-N-I was used to treat the lake water without
pH adjustment. After first adsorption, the spent adsorbent was collected via vacuum filtration and dried
overnight at 40 °C. The kinetics of desorption was studied with three desorption solutions, deionized water,

3 mM NaOH, and 30 mM NaOH at several time intervals between 1 min to 24 h. The batch tests were conducted on a shaker at 150 rpm and at room temperature, using 50 mL desorption solution and 0.25 g/L spent adsorbent. After desorption, the adsorbent was collected and dried at 40 °C overnight to be used for re-adsorption in a similar condition as the first adsorption. Desorption is determined as follows:

220 Desorption % =
$$\frac{C_{des}}{C_i - C_{ads}} \times 100$$
 (3)

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222 where C_{ads} is the COD_{Mn} after first adsorption, and C_{des} is the COD_{Mn} after desorption.

223 2.7. Theoretical analyses

The isotherms and kinetics of adsorption were analyzed via non-linear regression. We used Langmuir [22], Freundlich [23], and Sips [24] isotherm models and Lagergren's pseudo-first order [25] and pseudo-second order [26] kinetic models (see Table 1 in [20] for the equations). Weber and Morris intra-particle diffusion model [27] was used to explore the diffusion mechanisms involved in NOM adsorption (see Table 1 in [20]). The coefficient of determination, r^2 , and normalized standard deviation, Δq , (see Table 1 in [20]) were used to find the best-fitting nonlinear model and to quantitatively compare the applicability of the models.

Results and discussion
 3.1. Characteristics of the adsorbents
 3.1.1. Infrared spectroscopy

235 The FT-IR spectra of the initial and tailored materials are given Figure 1a. The spectra of the pinecone and the pristine biochar showed several significant bands. The bands at 3400-3300 cm⁻¹ correspond to O-H 236 stretching, at 2920 cm⁻¹ and 2870 cm⁻¹ indicate asymmetric and symmetric C-H, at 1600 cm⁻¹ are related to 237 238 C=C stretching, at 1240 cm⁻¹ are for C-O stretching, and at 1010 cm⁻¹ indicate C-H out-of-plane bending (e.g. 239 aromatic structure of lignin) [15, 28]. No characteristic band was observed for the TBs, confirming the 240 gasification and conversion to graphitic structure. For instance, the disappearance of O-H stretching vibration 241 bands for all the tailored materials suggests the oxygen in the initial materials was removed during fabrication 242 and phenolic-aromatic structures were cracked to leave carbon solids [28]. Similar results have been reported 243 on pinewood biochar [15].

Figure 1

245 3.1.2. Thermogravimetric and elemental analyses 246 247 The mass variation of the adsorbent materials as a function of temperature (TGA) is shown in Figure 1b. TGA 248 confirmed a high thermal stability of the tailored biochars. Three stages can be distinguished during the 249 pyrolysis of lignocellulosic materials, also observed for the pinecone biomass in Figure 3a in the reference 250 [20]. They include (I) dehydration below 150 °C, (II) primary pyrolysis between 200 to 480 °C with evolution 251 of most gases and tars and the formation of the basic structure via decomposition of hemicellulose and 252 cellulose, and (III) consolidation of the biochar structure at 500-800 °C with a small weight loss via 253 devolatilization of residual char and lignin [5, 29]. The pristine biochar also went through a large mass loss 254 between 300 °C and 500 °C. Compared with the biomass and pristine biochar, the tailored biochar showed 255 high thermal stability. The elemental analysis of the tailored biochar (TB-N-I) (see Figure 3c in [20]) confirmed 256 that TB-N-I consists mainly of carbon (84 wt. %) and other elements including oxygen (1.6 wt. %) and nitrogen 257 (12.7 wt. %) in minor contents.

258 259

3.1.3. Surface area and pore size distribution

260 Specific surface area and porosity are among the key properties of adsorptive materials. Table 2 compiles the 261 BET surface area, pore volume, and pore size of the initial and tailored materials. The biomass and pristine 262 biochar (B-300) have low specific surface areas, 0.491 m²/g and 0.583 m²/g, and pore volume, 0.001 and 263 0.001 cm³/g, respectively. This may be due to the presence of hemicellulose, cellulose, and lignin in the tight 264 structure of the initial materials. Since B-300 was pyrolyzed at relatively low temperature (300 °C), the 265 lignocellulosic framework was partially degraded resulting negligible increase in surface area and pore volume. The biochars tailored through both fabrication pathways, TB-N-I and TB-Z-II, showed remarkable 266 267 increase in specific surface area, 1470.3 and 1067.9 m²/g, and pore volume, 0.705 and 0.511 cm³/g, which 268 were higher than those of commercial PAC, 819.475 m²/g and 0.325 cm³/g, respectively. Chemical activation 269 enhances pore development and builds new pores, with elevated BET surface area upon increasing the post-270 pyrolysis temperature [9].

Table 2

272 273 The nitrogen gas adsorption–desorption isotherms results are depicted in Figure 1c. The shape of adsorption 274 isotherm discloses qualitative information about the adsorption mechanism and the pore structure of the 275 materials [10]. Adsorption isotherms of the biomass and pristine biochar show characteristics of type II 276 isotherm, indicating adsorption onto macroporous materials with strong adsorbate-adsorbent interactions. 277 Further, the isotherm curves remained unclosed at lower relative pressure region (see Figure 3b in [20]), 278 resulted from capillary condensation phenomenon. Chemisorption at a certain number of pores with strong 279 chemical potential may prevent desorption of the adsorbed nitrogen at low pressure [10]. The shape of the 280 N₂ adsorption-desorption isotherms along with low surface area and pore volume indicates that the biomass 281 and the pristine biochar provide limited pores. The isotherms of TBs show a predominantly mesoporous 282 structure of the developed carbons, resulting in a gradual increase in adsorption after the initial filling of the micropores, followed by an enhancement near saturation. They can be classified as a combination of type I 283 284 and type IV isotherms with hysteresis loops appeared at higher relative pressure region, indicating the wide 285 mesopore distribution in the materials [10, 13]. The development of highly mesoporous structure along with 286 some degree of micropores for the tailored biochars is further confirmed by the pore size distributions shown 287 in Figure 1d.

288

289

Figure 1

290 The pore size distribution of the tailored biochars mainly ranged within 2 nm to 10 nm, with the average pore 291 diameters of 2.96 and 2.68 nm for TB-N-I and TB-Z-II, respectively, confirming mesoporous characteristics 292 (Table 2). The porous materials can include three categories of micropores (< 2 nm), mesopores (2-50 nm) 293 and macropores (> 50 nm). Both micro-pores and meso-pores contents are enhanced in the modified 294 biochars compared to those of the biomass and the pristine biochar. The tailored biochars contain both 295 mesopores and micropores, yet the volume of mesopores was larger than that of micropores. The TBs benefit 296 from the mesoporous structure with higher surface area and narrower pore size distribution, providing high 297 accessibility for higher molecular weight NOM fraction and wider transport channels to micropores for the

lower molecular weight components of NOM (LMM). The mesoporous structure of the TBs is confirmed by
 SEM images in Figure 1e, which show the presence of microspores and mesopores. Table 3 compares the
 characteristics of biochars developed from forestry and agricultural wastes for pollutant removal.

301

304

Table 3

302 3.2. Adsorption of NOM and color from lake water

303 3.2.1. Dosage of adsorptive materials

305 Figure 2 shows NOM and color removal upon dosing of the adsorbents. The biomass and two pristine biochars 306 were unsuccessful in removing both NOM and color from the lake water samples (removal percentage < 25 307 %). A remarkable improvement was observed in the adsorption of NOM and color by all tailored biochars: 308 the removal increased with dosage. TB-N-I exhibited almost 300 % improvement in NOM adsorption from 309 lake water compared with those of the biomass and pristine biochars. An increase from 0.2 to 1 g/L of TB-N-310 I dosage improved the NOM removal from 76 % to 87 % and the color removal from 77 % to 93 %, 311 respectively. Alkali activated biochars generally provided higher efficiency for removing target contaminants 312 from the lake water. Compared with PAC, TB-N-I performed noticeably better, in lower doses e.g. 0.2 g/L TB-313 N-I removed 76% NOM compared with 60 % removal by 0.2 g/L PCA. The adsorption of NOM molecules 314 primarily occurs via physisorption e.g., pore filling and hydrophobic attraction through π - π electron donoracceptor [1], which are promoted by improved surface and pore characteristics of our tailored biochars 315 (Table 2). Higher NOM removal yields from both higher surface area and mesoporosity and the larger amount 316 317 of hydroxyl groups generated by alkali activation [7].

318

319

Figure 2

TB-N-I provided the highest adsorption percentage (80 %) and capacity (36 mg/g) with the lowest optimized dose (0.25 g/L) that were superior to those obtained by PAC (75%; 27 mg/g; 0.3 g/L). The optimized adsorbent dosage is illustrated in Figure 4a in reference [20]. Furthermore, Figure 2c shows the effect of concentration (dilutions of lake water) on NOM removal by 0.25 g/L TB-N-I at three contact times, viz. 0.5 min, 30 min, and 1440 min. The TB-N-I was able to effectively remove NOM from lake water across NOM concentrations. For 325 instance, after 1440 min of contact time, 72 % (9.97 mg/g) and 83 % (2.63 mg/g) of NOM were removed from 326 10 and 2.5 mg/L initial concentrations, respectively.

327 3.2.2. Water pH

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329 The characteristics of the pollutant, the adsorbent and the water matrix define the interface chemistry [30-330 32]. The pore size distribution plays a key role in NOM uptake, yet electrostatic attraction serves as the 331 secondary controlling factor [17]. NOM and color adsorption from the lake water were examined by varying 332 pH in the 2-10 range. As shown in Figure 3, the removal of both NOM and color by the engineered adsorbents 333 generally increased upon decreasing pH. The highest removal was achieved by TB-N-I with 97% NOM and 334 97% color removal at pH 2 while these amounts deceased to 73% NOM and 70% color removal at pH 10. A 335 lower pH-dependency was observed for the adsorption of NOM onto TB-N-I compared with that of PAC. A 336 higher pH-sensitivity was observed for the color adsorption compared with NOM adsorption, which can be 337 an indicative for the ionic nature of color causing compounds in lake water (Figure 3). These are promising 338 results in practical perspective, indicating the potential of our tailored biochars for effective NOM removal in a wide range of pH (with or without pH adjustment). 339

340

341

Figure 3

342 The solution pH regulates the protonation and deprotonation of both NOM fractions and biochars. While at lower pH, the attraction between protonated surface and the dissociated carboxylic group ($pK_a \sim 3$) accounts 343 344 for the adsorption of humic substances, at relatively higher pH the interaction between adsorbent and 345 neutral phenolic group (pK_a~ 9) dominates [33]. The surface of the tailored biochars shows an amphoteric 346 character. The point of zero charge (pH_{PZC}) for activated carbons and biochars has been reported around 7 to 347 8.5 [34, 35], which is consistent with the pH shift observed during our pH study (see Figure 4b in [20]). The 348 surface is positively charged at pH 2, partly due to the donor/acceptor interactions between the char 349 structure and the hydronium ions [35]. As there is a lower repulsion between NOM molecules adsorbed on 350 the surface and in the solution, the humic substances can pack closely on the surface. A declining adsorption 351 upon increasing pH suggests the electrostatic attraction being superior to the hydrogen bonding mechanism

352 [35]. Herein, the decreasing adsorption from pH 2 to 6 is caused by the progressively deprotonated surface 353 towards becoming uncharged, lowering the electrostatic interactions. As pH increases from 6 to 10 (Figure 354 3), the surface protonation is reduced and the hydrogen bonding become gradually dominant. Furthermore, 355 because of their relatively low charged character and physical intermolecular interactions e.g., Van der Waals 356 forces, humic substances aggregates at lower pH values, yielding a higher thickness and adsorbed NOM mass. 357 By raising pH, the charge density on the humic macromolecules increases due to the ionization of their acidic groups, which leads to intra- and intermolecular electrostatic repulsion. Consequently, the NOM 358 359 macromolecules gradually become non-aggregated, causing a thinner NOM layer thickness and lower 360 adsorbed mass [36].

361 3.2.3. Kinetics

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Figure 4 shows NOM and color removal by the TBs at different time intervals. The adsorption proceeds in two stages: a rapid uptake of the molecules within first 60 min, with 74.3 % and 59 % NOM removals by TB-N-I and PAC, respectively. A slower stage appears afterwards until the equilibrium is reached within 360 min, corresponding to 80.8 % removal by TB-N-I and 71.2 % removal by PAC. Similarly, color removal increased with contact time with the TBs.

Figure 4

When comparing the pseudo kinetic models, the experimental kinetic data showed a better fit to pseudosecond-order model (according to r² and Δ q values in Table 4). In nonlinear regression, a high value for the determination coefficient (r²) together with a small value for normalized standard deviation (Δ q) suggest good fitting of a model to experimental data [30, 37]. For all our studied cases, pseudo-second-order provided higher r² values and smaller Δ q values (e.g. r²= 0.814 and Δ q=0.124 for TB-N-I) compared with those of pseudo-first-order model (e.g., r²= 0.667 and Δ q=0.161 for TB-N-I).

376

The diffusion mechanisms of adsorption were studied by intra-particle diffusion model. As depicted in Figure 5a, the graphs of q_t versus $t^{1/2}$ are multi-linear including at least two linear stages. Adsorption proceeds in four consecutive steps [38] including film diffusion through the boundary layer to the external surface and the intraparticle diffusion (pore and surface diffusions) into the interior of the adsorbent. The total rate of adsorption is generally determined by film and/or intraparticle diffusions. The molecule transfer within the interior of the adsorbent normally occurs by pore and surface diffusions, yet their magnitudes are hardly determined. Thus, only a general intraparticle diffusion mechanism is assumed as predominant [38]. The multi-linearity of Figure 5a and C values in Table 4 suggest that the intraparticle diffusion is one of the stages involved in the NOM adsorption [30]. Film diffusion is the rate controlling stage in the initial NOM adsorption onto the exterior surface, afterwards proceeding by intra-particle diffusion into the pores.

387

389

Table 4

388 3.2.4. Isotherm

Adsorption isotherms determine the distribution of NOM molecules between the surface and solution at equilibrium. NOM adsorption isotherms are shown in Figure 5b. The adsorption increases sharply with increasing NOM equilibrium concentration, which is indicative of numerous readily accessible adsorption sites. Moreover, higher NOM adsorption is observed for TB-N-I compared with that of PAC.

394

Figure 5

395

The equilibrium data are modeled by nonlinear Langmuir, Freundlich, and Sips isotherms. Freundlich and Sips isotherms described the adsorption equilibrium data slightly better in terms of giving higher values for r^2 and lower values for Δq (Table 5). This suggests the heterogeneous distribution of the available active sites at the solid surface and the multilayer nature of adsorption. The Sips isotherm relates systems where one adsorbed molecule can get involved with more than one adsorptive site [30, 37].

401

403

Table 5

402 3.2.5. Removal mechanism

404 Characterization of NOM gives important information on the quality of the raw and treated water along with 405 the process performance. NOM in water can be characterized by e.g., degree of aromaticity, amino acid 406 content, and molar mass [18]. NOM fractions in both lake water and treated water samples were 407 characterized by LC-OCD analysis and the results are given in Table 6 and Figure 6.

408

Table 6

410 LC-OCD detected different NOM fractions, such as HMM humic substances and LMM organic acids. LC-OCD 411 results in Table 6 show that both TB-N-I and PAC, have effectively removed humic substances (HS) and 412 building blocks: 74.0% and 74.0% removals for TB-N-I and 59.8% and 68.9% for PAC, respectively. 413 Biopolymers were not retained as well; PAC was able to remove only 24.3 % while TB-N-I retained 61.1%. As NOM adsorption primarily takes place in mesopores and large micropores (1-2 nm width) [39, 40], these 414 results again suggest that TB-N-I has better range in pore size (consistent with the BET results in Table 2). 415 416 DOC uptake from lake water (Table 1) for PAC was approximately 81% of that obtained by TB-N-I. Table 6 417 also presents the average molar mass (MM) of HS, which increases from raw water sample to water samples 418 treated by PAC and TB-N-I, respectively. Accretion in average MM indicates that IMM and LMM compounds 419 are removed more effectively than HMM compounds. Consequently, TB-N-I is more efficient in removing 420 small size HS compared with PAC. These results confirm that the adsorbability of NOM increases with 421 decreasing molecular size, as suggested by Velten et al. [17] (i.e. biopolymers < HS < building blocks < LMM 422 compounds). With LMM compounds, however, there is a clear difference between LMM neutrals and LMM 423 acids. LMM neutrals, which are weakly or uncharged hydrophilic or slightly hydrophobic ("amphiphilic") 424 compounds, are retained well by both adsorbents (77.7% and 58.3% for TB-N-I and PAC, respectively). On 425 the other hand, the concentration of LMM acids, fraction containing all aliphatic organic acids, increases with 426 both PAC and TB-N-I treatment. As NOM with MM < 500 mg/l produces significant amount of disinfection 427 by-products [41, 42], their efficient removal is desirable. In this study, TB-N-I has removed 20% more LMM 428 NOM, including building blocks, LMM neutrals, and LMM acids, compared to PAC.

429

430

Figure 6

431 Chromatograms eluted for organic carbon (OC) and UV detection from LC-OCD analyses are shown in Figure 432 6 for raw and treated water samples with TB-N-I and PAC. The chromatogram for OC exhibits a peak for 433 biopolymers followed by large peak for humic substances and building blocks of humic substances. LMM 434 organics include both LMM acids and LMM humics, latter ones are later subtracted. Compared to the 435 chromatogram obtained with OC detection, that obtained with UV detection shows that TB-N-I treatment has retained more UV absorbing compounds than total NOM removal. Relative signal strength for raw water
is higher for UV compared to OC, while it is lower for PAC effluents.

438

439 The effective adsorption of NOM by our mesoporous biochars is mainly owing to the high surface area, meso-440 porosity, and large hydroxyl group contents generated by alkali activation. Our high temperature derived biochars also provide high surface aromaticity for a higher NOM sorption. Nevertheless, the nature and 441 442 functionality of the target organic compounds also affect their affinity for adsorption onto the TBs. The 443 mechanisms involved in NOM adsorption are explored in terms of multicomponent adsorption of its different 444 fractions. While polar fraction is removed by hydrogen bonding with the surface functional groups of the TBs, 445 non-polar fraction is attracted through hydrophobicity [1]. Furthermore, depending to the water chemistry, 446 the amphoteric surface of TBs gets positively or negatively charged causing electrostatic forces for charged 447 organic compounds. Aromatic π -systems in biochars provide high content of electron-withdrawing functional 448 groups, acting as π-acceptors for electron donors [1]. Both electron -rich and -poor functional groups are 449 present in high temperature derived biochars, enabling interactions with both electron donors and electron 450 accepters. At acidic environment, the π - π electron donor-acceptor interactions between π -electron -rich 451 surface and π -electron deficient organic compounds take place. At alkaline medium, adsorption is involved 452 with proton exchange with water and formation of hydrogen bonds between the organic compounds and a 453 surface carboxylate or phenolate, classified as a negative charge-assisted hydrogen-bond [43].

454

455 Figure 7 illustrate the dominant mechanisms contributing for the adsorption of NOM, including pore filling, 456 $\pi-\pi$ interactions, polar/electrostatic interactions, and hydrogen-bonding [1, 44]. However, the relative 457 contribution of these mechanisms to total adsorption is under debate. The more hydrophobic humic 458 substances attach to the mostly π -rich adsorptive sites so that hydrophobic interactions, e.g. π - π 459 interactions, contribute for the higher adsorption. However, the adsorption of hydrophilic LMM, e.g. tannic 460 acid, is accompanied with their smaller molecular size and easier reach to the inner meso- and micro-pores. 461 The relatively π -poor LMM fraction contain hydrophilic functional groups, e.g., digallic acid, enabling a 462 monolayer adsorption. Contrarily, the π -rich humic macromolecules with structural benzene rings can pile

463 up at the preoccupied adsorptive surface with humic compounds [4]. Nevertheless, diverse polar functional 464 groups on the structure of these compounds increase the adsorption affinity via hydrogen bonds and polar 465 interactions with the engineered surface. Thus, there is more multi-layer adsorption onto mesoporous TB-N-466 I than microporous PAC. In summary, higher adsorption of NOM onto TB-N-I originates from the presence of 467 more adsorptive sites through meso-porosity, high aromatic surface area, and alkali-generated hydroxyl 468 groups, resulting in the higher adsorption affinity of LMM NOM than those provided by the microporous PAC.

469

Figure 7

470 471

3.3. Desorption-re-adsorption

472 To study the chemical regeneration potential, the desorption process on the spent tailored biochars was 473 performed in three regeneration systems, e.g. distilled water, 3 mM NaOH and 30 mM NaOH (see Figure 5 in 474 [20]). The desorbed NOM concentrations at several time intervals were determined. The desorption 475 increased at higher alkaline medium as 30 mM NaOH > 3 mM NaOH > distilled water. It was also observed 476 that desorption increases upon increasing time: up to 62 % desorption was achieved within 3 h, afterwards 477 gradually raised up to 70 % within 24 h. These results indicate the adsorption of NOM onto TB-N-I is mostly 478 reversible and the spent adsorbents show high capacity for regeneration. The second cycle of NOM 479 adsorption on regenerated TB-N-I was performed at different time intervals. It was observed that re-480 adsorption increased by time (see Figure 5b in [20]). The adsorption capacity of virgin TB-N-I within 3 h of contact time was around 12.5 mg/g, while NOM adsorption on the regenerated TB-N-I amounted 13.8 mg 481 482 /g. The regenerated TB-N-I possessed a high adsorption capacity and hence could be utilized repeatedly for 483 NOM adsorption.

484 4. Conclusions

485

486 Natural organic matter (NOM) in drinking water treatment serves as precursors to disinfection by-products 487 (DBPs) and promotes microbial regrowth in the water distribution system. Renewable pinecone biomass has 488 been used to tailor mesoporous biochars for removing NOM from lake water. The adsorbents were fabricated 489 via pre-pyrolysis/activation/post-pyrolysis and activation/post-pyrolysis processes, using chemical activators

490 to enhance the surface chemistry and porous structure for a higher NOM uptake. Characterization analyses e.g. BET, SEM, EDX, FTIR, and TGA revealed high thermal stability, mesoporous structure, remarkable surface 491 area (up to 1470 m^2/g), elevated carbon content and surface functionality of the engineered products. Our 492 tailored biochars showed superior removal capacities for NOM and color from lake water compared with 493 494 those of the biomass and pristine biochars. The most promising tailored biochar (TB-N-I) was prepared via 495 NaOH activation accompanied with pre- and post-pyrolysis. With lowest 0.25 g/L dosage, TB-N-I removed 496 more than 80 % of both NOM and color, a superior removal capacity compared to that of commercial 497 activated carbon (PAC). Effective NOM and color removals were achieved under a wide pH-range, e.g. TB-N-498 I removed 97 % of NOM at pH 2. Nonlinear regression showed good fits for Freundlich and Sips isotherm and 499 pseudo-second-order kinetic models with the experimental data. Higher alkaline mediums (30 mM NaOH > 500 3 mM NaOH > distilled water) provided higher desorption resulting in regenerated adsorbents with large re-501 adsorption capacities. Liquid chromatograph-organic carbon detection (LC-OCD) detected different NOM 502 fraction in the lake water and was used for enlightening the mechanisms involved in NOM adsorption. LC-503 OCD results suggested that TB-N-I was more effective in removing the problematic low molar mass (LMM) 504 compounds compared to PAC. In summary, the experimental results and theoretical analyses confirm the 505 high potential for the applicability of our tailored biochars for NOM treatment.

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507

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- Table content:
- Table 1. Characteristics of the lake water.
- Table 2. BET analysis values.
- Table 3. Engineered materials developed from forestry and agricultural wastes for pollutant removal.
- Table 4. Calculated kinetic parameters for the adsorption of NOM.
- Table 5. Adsorption isotherm parameters for the adsorption of NOM calculated via nonlinear regression.
- Table 6. Average results and standard deviation of LC-OCD analysis for raw lake water and PAC and TB-N-I effluents.
- MM denotes molar mass.

Table 1. Characteristics of the lake water.

| Parameter | Raw | Treated with TB-N-I |
|---------------------------|-------|---------------------|
| рН | 7.82 | 7.19 |
| Conductivity [mS/cm] | 0.206 | 0.224 |
| Turbidity [FNU] | 8.50 | 4.52 |
| Color [mg/l Pt] | 53.65 | 10.68 |
| COD _{Mn} | 13.4 | 4.38 |
| NPOC | 16.51 | 5.536 |
| Total nitrogen [mg/l N] | 4.2 | 1.49 |
| Total phosphorus [µg/l P] | 151 | 104 |

Table 2. BET analysis values.

| Materials | BET surface area [m²/g] | Pore volume [cm³/g] | Pore size [nm] |
|-----------|----------------------------|------------------------|-------------------|
| Biomass | 0.491 | 0.001 | 9.262 |
| B-300 | 0.583 | 0.001 | 7.400 |
| TB-N-I | 1470.266 | 0.705 | 2.959 |
| TB-Z-II | 1067.902 | 0.511 | 2.681 |
| PAC | 819.475 | 0.325 | 4.291 |

Note: Adsorption cumulative isotherms were used to determine pore volume and pore size distribution via the Barret-Joyner-Halender (BJH) methodology.

| 758 | Table 3. Engineered materials development | oped from forestry and agricult | ural wastes for pollutant removal. |
|-----|---|---------------------------------|------------------------------------|
| | | | |

| Adsorptive material | Initial material | Surface area (m²/g) | Pore volume (cm³/g) | Pollutant | Sorption (mg/g) | Ref. |
|--|---------------------------|------------------------|------------------------|----------------------------------|--------------------|-----------|
| Acid/alkali- modified biochars | rice-husk | 46.8, 117.8 | 0.033, 0.073 | tetracycline | 58.8 | [11] |
| MgO-impregnated biochar | sugarcane crop residue | 40.6-218.9 | 0.37-0.06 | phosphate, ammonium humate | 398 22 247 | [12] |
| ZnCl ₂ - activated biochar | biogas residue | 516.67 | 0.24 | arsenite | 27.67 | [13] |
| Biochar | wood and sludge | 400 | - | sulfamethoxazole antibiotic | - | [6] |
| Biochar microparticles | pig manure | - | - | methylene blue | 25 | [14] |
| Activated Biochar | pinewood | 852.95 | - | chlortetracycline | 208.3 | [15] |
| Tailored mesoporous biochar | pinecone | 1470 | 0.705 | NOM | 36 | this work |

Table 4. Calculated kinetic parameters for the adsorption of NOM.

| | Material | q _{e(exp)} | Pseudo | o-first-orc | -order Pseudo-second-order | | | Intraparticle diffusion | | | | | |
|---|----------|---------------------|----------------------------|-------------|----------------------------|-------|-----------------|-------------------------|-------|-------|-----------------|-------|---|
| | | | q _{e(cal)} | k1 | r ² | Δq | q e(cal) | k ₂ | r² | Δq | k _{ip} | | С |
| | | | | Nonlinear | | | | | | Line | ar | | |
| - | TB-N-I | 38.15 | 33.16 | 0.629 | 0.667 | 0.161 | 34.85 | 0.023 | 0.814 | 0.124 | 0.411 | 25.65 | |
| | TB-N-II | 18.16 | 14.13 | 0.817 | 0.588 | 0.182 | 14.71 | 0.080 | 0.655 | 0.153 | 0.183 | 11.04 | |
| - | TB-Z-II | 14.45 | 11.76 | 0.092 | 0.655 | 1.333 | 12.24 | 0.013 | 0.753 | 0.684 | 0.253 | 6.06 | |

Table 5. Adsorption isotherm parameters for the adsorption of NOM calculated via nonlinear regression.

| Model | Material | Parameter | | | | | |
|------------|----------|---|-------------------------|----------------|----------------|-------|--|
| Langmuir | | q∟(mg/g) | K∟(L/mg) | r ² | Ĺ | 7d | |
| | TB-N-I | 180.24 | 0.064 | 0.953 | 0.373 | | |
| | PAC | 133.24 | 0.072 | 0.967 | 0.3 | 0.184 | |
| Freundlich | | K _F (mg/g)/(mg/L) ^{1/n} | 1/n | r ² | Ĺ | 7d | |
| | TB-N-I | 9.446 | 0.985 | 0.984 | 0.0 | 081 | |
| | PAC | 9.763 | 0.795 | 0.965 | 0.3 | 189 | |
| Sips | | qs (mg/g) | Ks (L/mg) ^{ns} | ns | r ² | Δq | |
| | TB-N-I | 143.97 | 0.058 | 1.330 | 0.988 | 0.080 | |
| | PAC | 127.99 | 0.075 | 1.012 | 0.967 | 0.103 | |

Table 6. Average results and standard deviation of LC-OCD analysis for raw lake water and PAC and TB-N-I effluents.
 MM denotes molar mass.

| | Chromato- | Bio- | Humic | MM of HS | Building | Low MM | Low MM |
|-----------|-------------|-----------|-------------|------------|------------|------------|------------|
| Sample | graphic DOC | polymers | Substances | | Blocks | Neutrals | Acids |
| | (µg/l) | (µg/l) | (HS) (µg/l) | (g/mol) | (µg/l) | (µg/l) | (µg/l) |
| Raw water | 10169 | 246 | 6921 | 534 | 1495 | 1450 | 57 |
| PAC | 4148 ± 19.3 | 187 ± 3.0 | 2784 ± 31.3 | 572 ± 13 | 465 ± 19.9 | 605 ± 12.3 | 106 ±15.3 |
| TB-N-I | 2732 ± 69.9 | 96 ± 0.8 | 1813 ± 53.5 | 656 ± 42.0 | 388 ± 74.4 | 324 ± 36.4 | 111 ± 13.3 |

- 908 Figure content:
- 909
 910 Figure 1. FTIR spectra (a) and TGA thermograms (b) of the tailored and initial materials. Nitrogen adsorption-desorption
 911 isotherms (c), pore size distribution (d), and SEM images of TB-N-I (e).
- **Figure 2.** NOM (a) and color (b) removal from lake water by varying adsorbent dosage after 24 h contact time. (c) NOM
- 913 removal at different dilutions by 0.25 g/L TB-N-I at 0.5, 30, and 1440 min contact times Experimental condition: room 914 temperature; natural pH.
- Figure 3. Effect of pH on NOM (a) and color (b) removals from lake water by the tailored and initial materials Experimental condition: optimized adsorbent dosage; 24 h contact time; room temperature.
- Figure 4. Effect of contact time on NOM (a) and color (b) removals from lake water by the tailored and initial materials
 Experimental condition: optimized adsorbent dosage; natural pH; room temperature.
- Figure 5. a) Intra-particle diffusion plots for NOM adsorption onto tailored biochars. b) Equilibrium experimental
 (markers) and theoretical data (lines) plotted via non-linear regression for NOM adsorption onto TB-N-I and PAC.
- Figure 6. LC-OCD chromatograms obtained with organic carbon detection (a) and UV detection (b) for influent and
 effluent samples of PAC and TB-N-I.
- Figure 7. Schematic illustration of key mechanisms involved in NOM adsorption from lake water by tailored mesoporousbiochars.







Figure 1. FTIR spectra (a) and TGA thermograms (b) of the tailored and initial materials. Nitrogen adsorption desorption isotherms (c), pore size distribution (d), and SEM images of TB-N-I (e).



Figure 2. NOM (a) and color (b) removal from lake water by varying adsorbent dosage after 24 h contact time. (c) NOM removal at different dilutions by 0.25 g/L TB-N-I at 0.5, 30, and 1440 min contact times - Experimental condition:

room temperature; natural pH.



Figure 3. Effect of pH on NOM (a) and color (b) removals from lake water by the tailored and initial materials Experimental condition: optimized adsorbent dosage; 24 h contact time; room temperature.





Figure 4. Effect of contact time on NOM (a) and color (b) removals from lake water by the tailored and initial materials - Experimental condition: optimized adsorbent dosage; natural pH; room temperature.







Figure 5. a) Intra-particle diffusion plots for NOM adsorption onto tailored biochars. b) Equilibrium experimental (markers) and theoretical data (lines) plotted via non-linear regression for NOM adsorption onto TB-N-I and PAC.





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