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1 **Tailored mesoporous biochar sorbents from pinecone biomass for the adsorption of natural**
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 by-
35 products for treating NOM and color causing compounds from drinking water sources, such as lakes. Herein,
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
50 adsorption, e.g., NOM removal by TB-N-I from the lake water reached 97 % at pH 2. Nonlinear regression
51 provided a good fit for Freundlich and Sips ($r^2= 0.988$ and $\Delta q=0.08$) 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
55 adsorbents with high re-adsorption capacity. Liquid chromatograph–organic carbon detection (LC-OCD) was
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.

61

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

63

1. Introduction

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 biomass via pyrolysis in a limited oxygen atmosphere results in biochar, bio-oil, and syngas [3, 4]. Biochar production from waste biomass is both economical and environmentally beneficial [1]. Owing to their porous structure, relatively high surface area, and enriched surface chemistry, there is a growing interest for biochars as sustainable media in engineering value-added materials [2]. They can be produced near the point of application and/or near biomass sources in both small-scale pyrolysis units and in large-scale integrated refinery facilities that are designed for simultaneous biochar and energy production.

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

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

113

114 Our objective is to tailor biochars with high content of mesopores accompanied with micropores and desired
115 surface functional groups through 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
123 characterization methods such as Brunauer, Emmett and Teller (BET) specific surface area/porosity,
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

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

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

140 2.2. Fabrication of mesoporous biochars

141
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
148 weight ratio of biochar/activator) for 2 h, dried overnight at 105 °C, and thirdly heated for 2 h under nitrogen
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 μ m 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).

157 2.3. Characterization of mesoporous biochars

158
159 Brunauer, Emmett and Teller (BET) specific surface area and porosity analysis was conducted using Tristar II-
160 Micromeritics, USA, via the adsorption-desorption cycle of N₂ gas at 77.350 K onto the external surface of

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

168 2.4. Raw water samples

169
170 Lake water samples were collected from Lake Pitkäjärvi in Espoo, Finland. Table 1 compiles the quality
171 characteristic of the lake water.

172 Table 1

173 2.4.1. NOM and color measurement

174
175 The concentration of NOM was estimated via UV absorbance measurement at 254 nm wavelength, using a
176 UV-1201 Shimadzu-spectrophotometer. The samples were filtered before the measurement through
177 Sartorius Minisart 0.45 μ m 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

185
186 Liquid chromatograph–organic carbon detection (LC-OCD) quantifies the elution as a function of size and
187 affinity of carbon from a Toyoperal HW 50 s column using a buffered carrier solution [21]. The method was

188 calibrated using Suwannee River humic and fulvic acid standards. UV254 absorbance and organic carbon
189 were measured online and allowed quantifying the elution of DOC over time. UV254 absorbance was
190 measured with a K200 detector by Knauer, organic carbon was measured by first decomposing it to carbon
191 dioxide (CO₂) in a Gräntzel-reactor and then measuring the CO₂ with Ultramat 6 infrared detector by Siemens.
192 FIFFIKUS software was used to separate the acquired chromatograph into different apparent size fractions,
193 viz. biopolymers (molecular weight (MW) > 20 kDa), humic substances (MW ~ 1000 Da), building blocks (MW
194 300-500 Da), low molecular weight acids (MW < 350 Da), and low molecular weight neutrals (MW < 350 Da).

195 2.5. Adsorption

196
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:

$$205 \text{ Removal \%} = \frac{(C_i - C_t)}{C_i} \times 100 \quad (1)$$

$$206 \text{ } q_t \text{ (mg/g)} = \frac{C_i - C_t}{m} \times V \quad (2)$$

207
208
209 where C_i and C_t (mg/L) are the initial COD_{Mn} concentration and the concentration at time t, respectively, V (L)
210 is solution volume, and m (g) is adsorbent mass.

211 2.6. Desorption and re-adsorption

212
213 For desorption and re-absorption batches, 0.25 g/L dosage of TB-N-I was used to treat the lake water without
214 pH adjustment. After first adsorption, the spent adsorbent was collected via vacuum filtration and dried
215 overnight at 40 °C. The kinetics of desorption was studied with three desorption solutions, deionized water,

216 3 mM NaOH, and 30 mM NaOH at several time intervals between 1 min to 24 h. The batch tests were
217 conducted on a shaker at 150 rpm and at room temperature, using 50 mL desorption solution and 0.25 g/L
218 spent adsorbent. After desorption, the adsorbent was collected and dried at 40 °C overnight to be used for
219 re-adsorption in a similar condition as the first adsorption. Desorption is determined as follows:

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

221
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

224
225 The isotherms and kinetics of adsorption were analyzed via non-linear regression. We used Langmuir [22],
226 Freundlich [23], and Sips [24] isotherm models and Lagergren's pseudo-first order [25] and pseudo-second
227 order [26] kinetic models (see Table 1 in [20] for the equations). Weber and Morris intra-particle diffusion
228 model [27] was used to explore the diffusion mechanisms involved in NOM adsorption (see Table 1 in [20]).
229 The coefficient of determination, r^2 , and normalized standard deviation, Δq , (see Table 1 in [20]) were used
230 to find the best-fitting nonlinear model and to quantitatively compare the applicability of the models.

231 3. Results and discussion

232 3.1. Characteristics of the adsorbents

233 3.1.1. Infrared spectroscopy

234
235 The FT-IR spectra of the initial and tailored materials are given Figure 1a. The spectra of the pinecone and
236 the pristine biochar showed several significant bands. The bands at 3400-3300 cm^{-1} correspond to O-H
237 stretching, at 2920 cm^{-1} and 2870 cm^{-1} indicate asymmetric and symmetric C-H, at 1600 cm^{-1} are related to
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].

244

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 3.1.3. Surface area and pore size distribution

259

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
266 volume. The biochars tailored through both fabrication pathways, TB-N-I and TB-Z-II, showed remarkable
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].

271

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
283 micropores, followed by an enhancement near saturation. They can be classified as a combination of type I
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

Figure 1

289

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

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

301 Table 3

302 3.2. Adsorption of NOM and color from lake water

303 3.2.1. Dosage of adsorptive materials

304

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 donor-
315 acceptor [1], which are promoted by improved surface and pore characteristics of our tailored biochars
316 (Table 2). Higher NOM removal yields from both higher surface area and mesoporosity and the larger amount
317 of hydroxyl groups generated by alkali activation [7].

318 Figure 2

319

320 TB-N-I provided the highest adsorption percentage (80 %) and capacity (36 mg/g) with the lowest optimized
321 dose (0.25 g/L) that were superior to those obtained by PAC (75%; 27 mg/g; 0.3 g/L). The optimized adsorbent
322 dosage is illustrated in Figure 4a in reference [20]. Furthermore, Figure 2c shows the effect of concentration
323 (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
324 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

328
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 decreased 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
339 a wide range of pH (with or without pH adjustment).

340 Figure 3

341
342 The solution pH regulates the protonation and deprotonation of both NOM fractions and biochars. While at
343 lower pH, the attraction between protonated surface and the dissociated carboxylic group ($pK_a \sim 3$) accounts
344 for the adsorption of humic substances, at relatively higher pH the interaction between adsorbent and
345 neutral phenolic group ($pK_a \sim 9$) 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
358 groups, which leads to intra- and intermolecular electrostatic repulsion. Consequently, the NOM
359 macromolecules gradually become non-aggregated, causing a thinner NOM layer thickness and lower
360 adsorbed mass [36].

361 3.2.3. Kinetics

362
363 Figure 4 shows NOM and color removal by the TBs at different time intervals. The adsorption proceeds in
364 two stages: a rapid uptake of the molecules within first 60 min, with 74.3 % and 59 % NOM removals by TB-
365 N-I and PAC, respectively. A slower stage appears afterwards until the equilibrium is reached within 360 min,
366 corresponding to 80.8 % removal by TB-N-I and 71.2 % removal by PAC. Similarly, color removal increased
367 with contact time with the TBs.

368 Figure 4

369
370 When comparing the pseudo kinetic models, the experimental kinetic data showed a better fit to pseudo-
371 second-order model (according to r^2 and Δq values in Table 4). In nonlinear regression, a high value for the
372 determination coefficient (r^2) together with a small value for normalized standard deviation (Δq) suggest
373 good fitting of a model to experimental data [30, 37]. For all our studied cases, pseudo-second-order
374 provided higher r^2 values and smaller Δq values (e.g. $r^2= 0.814$ and $\Delta q=0.124$ for TB-N-I) compared with those
375 of pseudo-first-order model (e.g., $r^2= 0.667$ and $\Delta q=0.161$ for TB-N-I).

376
377 The diffusion mechanisms of adsorption were studied by intra-particle diffusion model. As depicted in Figure
378 5a, the graphs of q_t versus $t^{1/2}$ are multi-linear including at least two linear stages. Adsorption proceeds in
379 four consecutive steps [38] including film diffusion through the boundary layer to the external surface and
380 the intraparticle diffusion (pore and surface diffusions) into the interior of the adsorbent. The total rate of

381 adsorption is generally determined by film and/or intraparticle diffusions. The molecule transfer within the
382 interior of the adsorbent normally occurs by pore and surface diffusions, yet their magnitudes are hardly
383 determined. Thus, only a general intraparticle diffusion mechanism is assumed as predominant [38]. The
384 multi-linearity of Figure 5a and C values in Table 4 suggest that the intraparticle diffusion is one of the stages
385 involved in the NOM adsorption [30]. Film diffusion is the rate controlling stage in the initial NOM adsorption
386 onto the exterior surface, afterwards proceeding by intra-particle diffusion into the pores.

387 Table 4

388 3.2.4. Isotherm

389

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

394 Figure 5

395

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

401 Table 5

402 3.2.5. Removal mechanism

403

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

409
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
414 NOM adsorption primarily takes place in mesopores and large micropores (1-2 nm width) [39, 40], these
415 results again suggest that TB-N-I has better range in pore size (consistent with the BET results in Table 2).
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

Figure 6

430

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

436 has retained more UV absorbing compounds than total NOM removal. Relative signal strength for raw water
437 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
441 biochars also provide high surface aromaticity for a higher NOM sorption. Nevertheless, the nature and
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 π - π 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 3.3. Desorption–re-adsorption

471

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
481 contact time was around 12.5 mg/g, while NOM adsorption on the regenerated TB-N-I amounted 13.8 mg
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
491 e.g. BET, SEM, EDX, FTIR, and TGA revealed high thermal stability, mesoporous structure, remarkable surface
492 area (up to 1470 m²/g), elevated carbon content and surface functionality of the engineered products. Our
493 tailored biochars showed superior removal capacities for NOM and color from lake water compared with
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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631 Table content:
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633 **Table 1.** Characteristics of the lake water.
634 **Table 2.** BET analysis values.
635 **Table 3.** Engineered materials developed from forestry and agricultural wastes for pollutant removal.
636 **Table 4.** Calculated kinetic parameters for the adsorption of NOM.
637 **Table 5.** Adsorption isotherm parameters for the adsorption of NOM calculated via nonlinear regression.
638 **Table 6.** Average results and standard deviation of LC-OCD analysis for raw lake water and PAC and TB-N-I effluents.
639 MM denotes molar mass.
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Table 1. Characteristics of the lake water.

Parameter	Raw	Treated with TB-N-I
pH	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

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758 **Table 3.** Engineered materials developed from forestry and agricultural wastes for pollutant removal.

Adsorptive material	Initial material	Surface area (m ² /g)	Pore volume (cm ³ /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

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

Material	$q_{e(\text{exp})}$	Pseudo-first-order			Pseudo-second-order				Intraparticle diffusion		
		$q_{e(\text{cal})}$	k_1	r^2	Δq	$q_{e(\text{cal})}$	k_2	r^2	Δq	Linear	
										k_{ip}	C
Nonlinear											
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

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

Model	Material	Parameter				
Langmuir		q_L (mg/g)	K_L (L/mg)	r^2	Δq	
	TB-N-I	180.24	0.064	0.953	0.373	
	PAC	133.24	0.072	0.967	0.184	
Freundlich		K_F (mg/g)/(mg/L) ^{1/n}	1/n	r^2	Δq	
	TB-N-I	9.446	0.985	0.984	0.081	
	PAC	9.763	0.795	0.965	0.189	
Sips		q_s (mg/g)	K_s (L/mg) ^{n_s}	n_s	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

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

Sample	Chromato-graphic DOC ($\mu\text{g/l}$)	Bio-polymers ($\mu\text{g/l}$)	Humic Substances (HS) ($\mu\text{g/l}$)	MM of HS (g/mol)	Building Blocks ($\mu\text{g/l}$)	Low MM Neutrals ($\mu\text{g/l}$)	Low MM Acids ($\mu\text{g/l}$)
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

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Figure content:

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.

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.

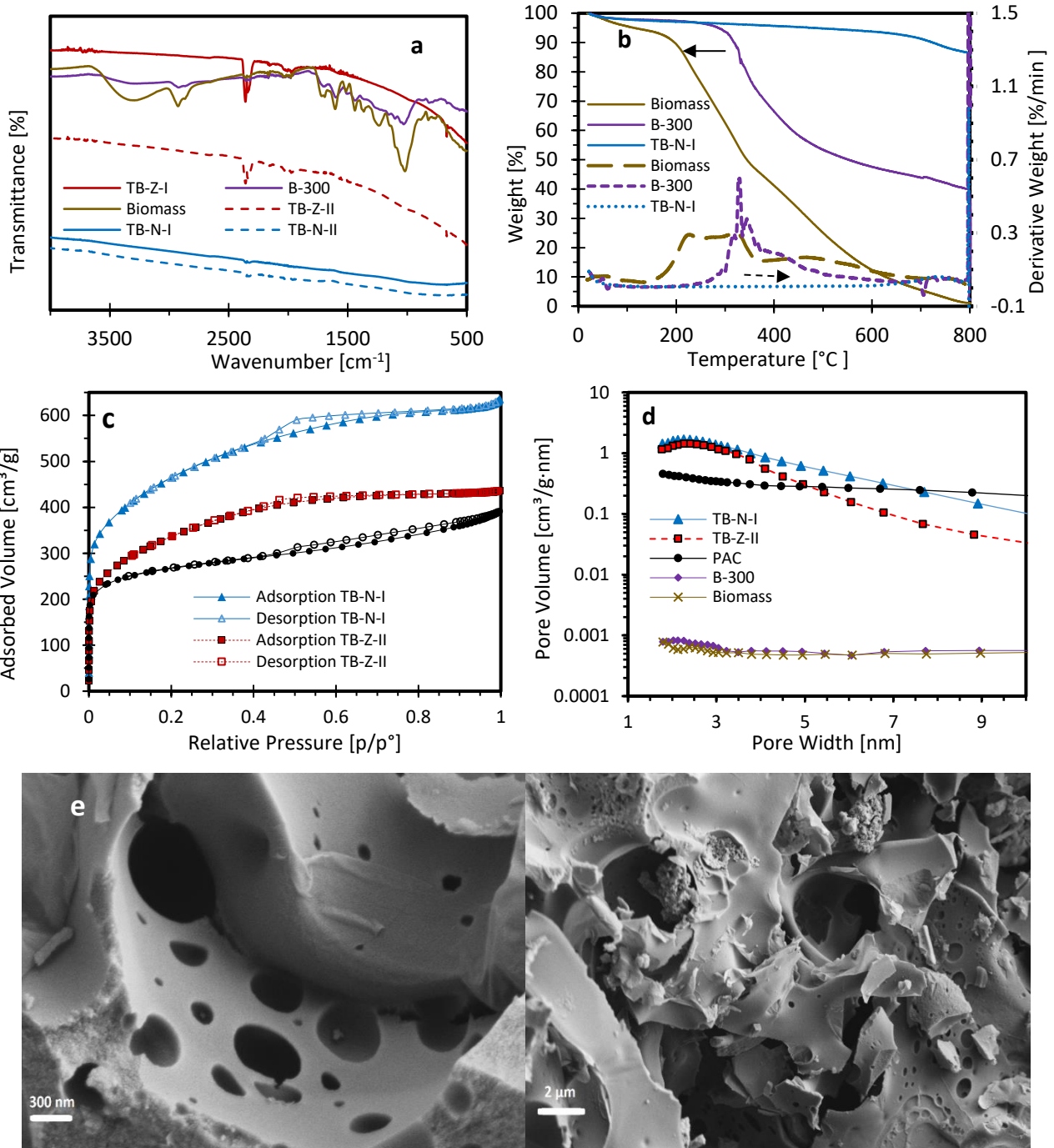
Figure 7. Schematic illustration of key mechanisms involved in NOM adsorption from lake water by tailored mesoporous biochars.

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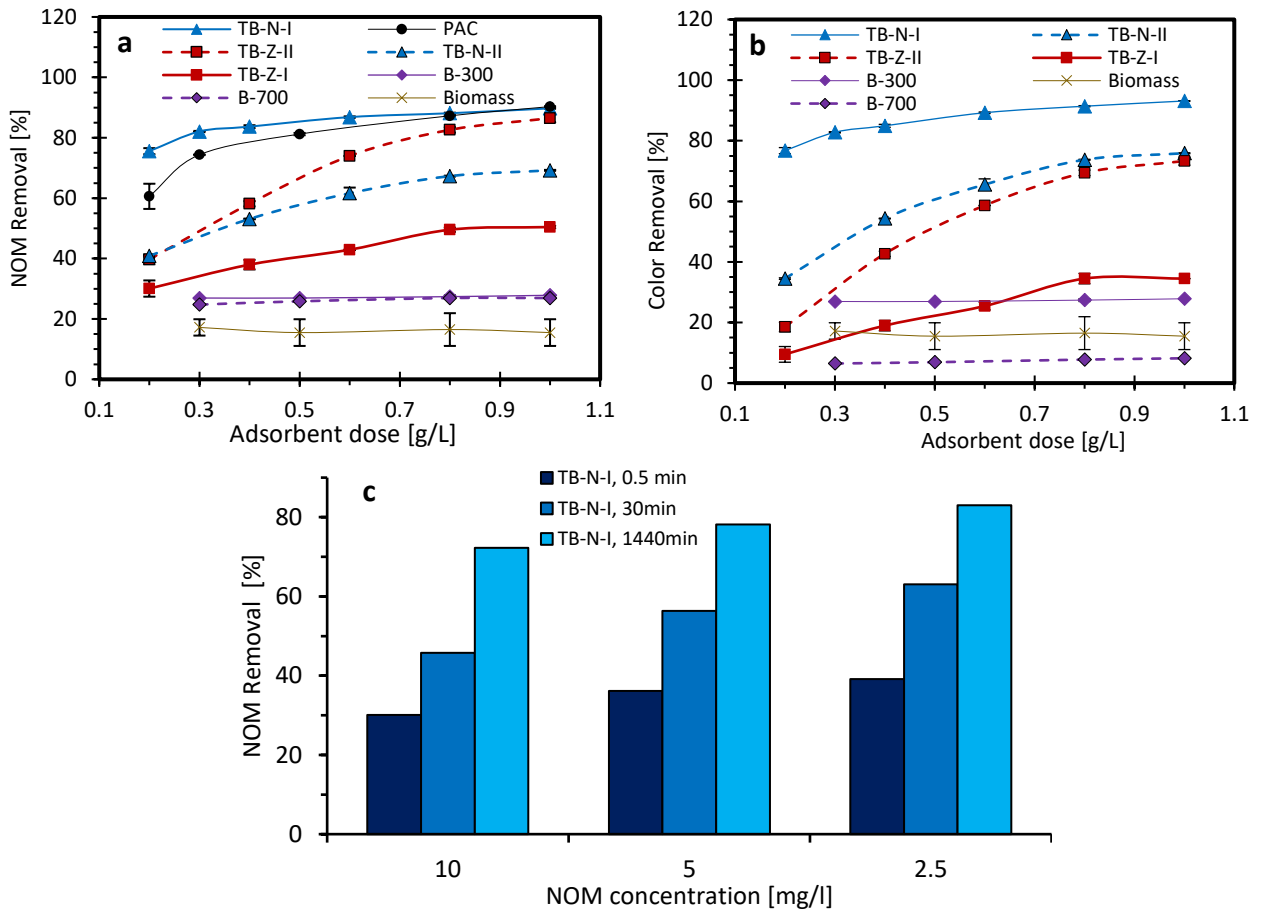
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Figure 1. FTIR spectra (a) and TGA thermograms (b) of the tailored and initial materials. Nitrogen adsorption-desorption isotherms (c), pore size distribution (d), and SEM images of TB-N-I (e).

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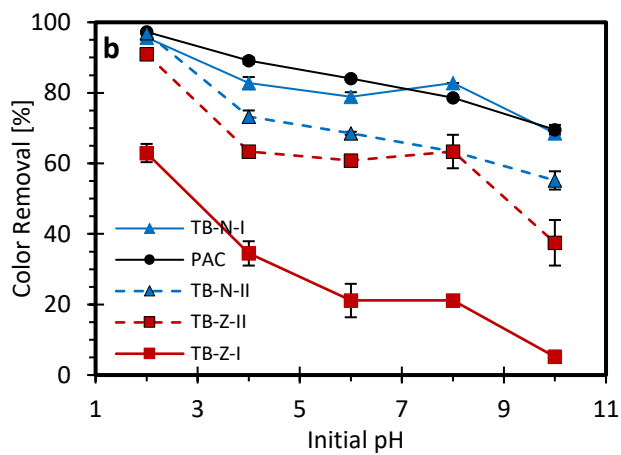
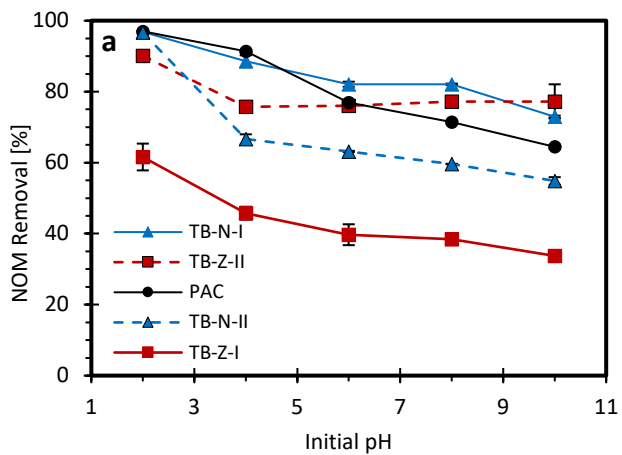


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972 **Figure 2.** NOM (a) and color (b) removal from lake water by varying adsorbent dosage after 24 h contact time. (c)
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 985 Experimental condition: optimized adsorbent dosage; 24 h contact time; room temperature.

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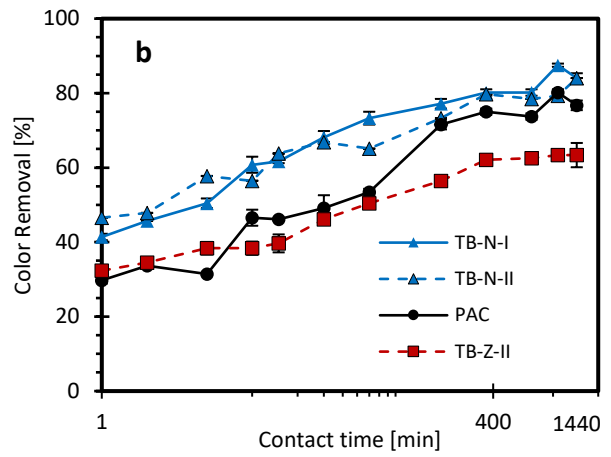
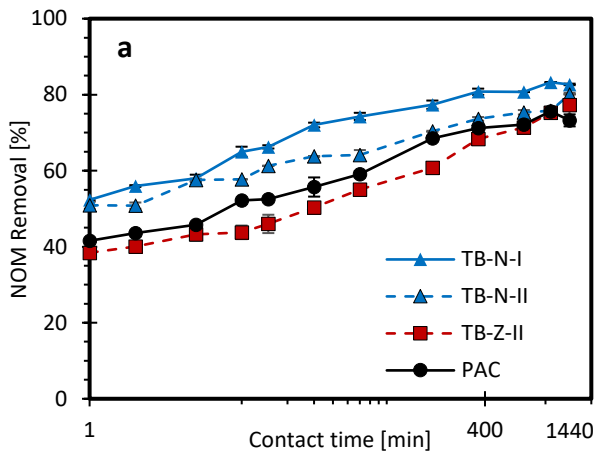
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1012 **Figure 4.** Effect of contact time on NOM (a) and color (b) removals from lake water by the tailored and initial materials
 1013 - Experimental condition: optimized adsorbent dosage; natural pH; room temperature.

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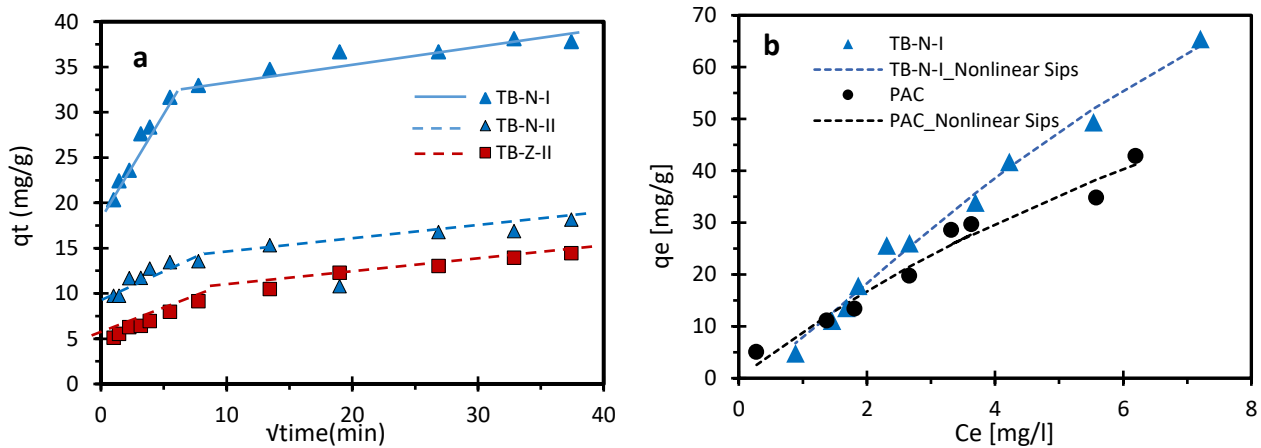
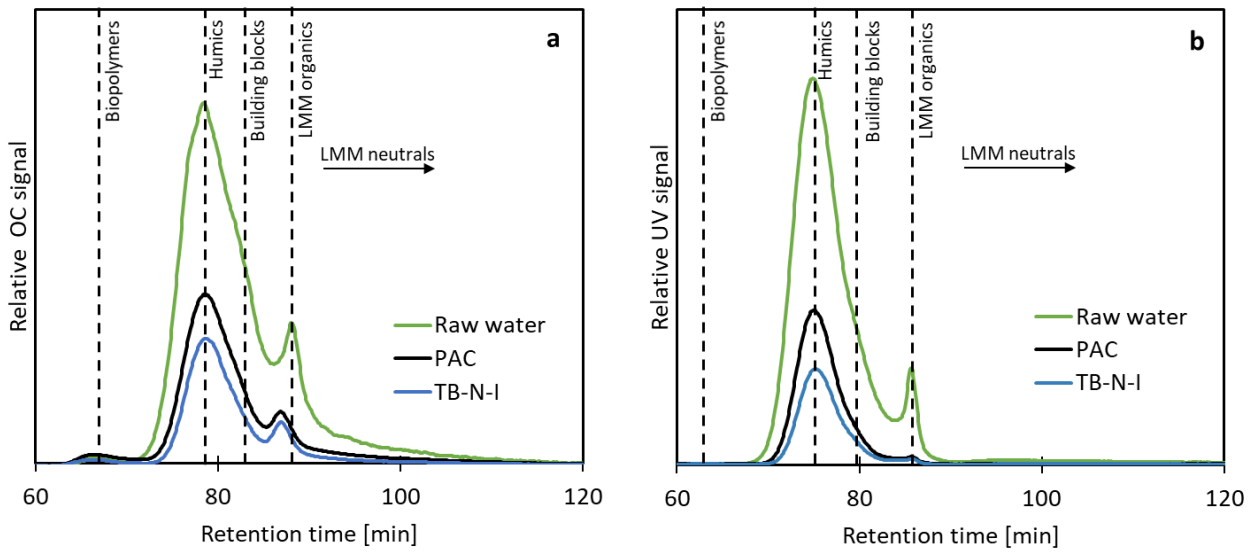


Figure 5. a) Intra-particle diffusion plots for NOM adsorption onto tailored biochars. b) Equilibrium experimental (markers) and theoretical data (lines) plotted via non-linear regression for NOM adsorption onto TB-N-I and PAC.

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1060 **Figure 6.** LC-OCD chromatograms obtained with organic carbon detection (a) and UV detection (b) for influent and
1061 effluent samples of PAC and TB-N-I.
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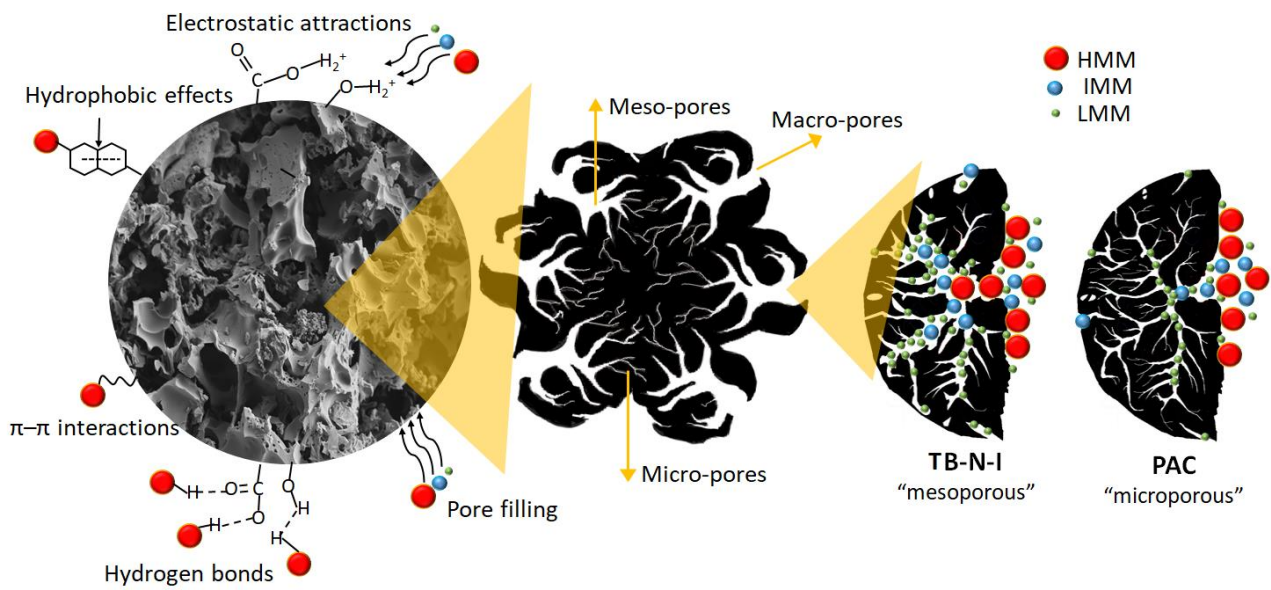
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