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Tailoring metal-impregnated biochars for selective removal of natural organic matter and dissolved phosphorus from the aqueous phase

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ABSTRACT

This study aimed to investigate how the production process of metal impregnated biochars (MIBs) affects their selectivity in the simultaneous adsorption of organic matter and dissolved phosphorus from the aqueous phase. MIBs were produced via a two-step pyrolysis procedure including impregnation of metal oxides in the structure of the softwood-derived biochars, resulting in copper-impregnated biochar (Cu-MIB) and iron-impregnated biochar (Fe-MIB). The tailoring process was conducted by optimization of pyrolysis temperature during the biochars production stage. The MIBs were characterized via advanced characterization analyses to acquire structural, elemental, and morphological properties of the adsorbent. The surface area of MIB (99 m²/g and 92 m²/g for Cu-MIB and Fe-MIB respectively) decreased compared to pristine biochar (571 m²/g), indicating a successful impregnation of metal oxide particles within the porous carbon structure. The effect of operational parameters on adsorption as well as selectivity tests were examined in the batch mode. The optimum doses for NOM removal were 2 g/l for Fe-MIB (96%) and 0.5 g/l for Cu-MIB (87%). For phosphorus removal, optimum doses were 1 g/l for Fe-MIB (95%) and 2 g/l for Cu-MIB (93%). The lower pH values favored adsorption for both MIBs. In the binary solution of NOM and phosphorus, the NOM was selectively adsorbed by the Cu-MIB, whereas phosphorus was selectively removed by the Fe-MIB. The results provide a deeper understanding of the tailoring process of biochars for producing new biochars as selective adsorbents for specific target pollutants.

1. Introduction

Natural organic matter (NOM) is a complex matrix of organic compounds with a wide range of molecular masses present in natural water sources. NOM raises aesthetic issues including unpleasant taste, odor, and color of the water. It significantly influences drinking water production by, for example, contributing to the membrane fouling, competing with the removal of other pollutants, increasing process costs, and causing microbial regrowth in the distribution system [1–3].

Phosphorus acts as a fundamental yet finite element for the growth of living organisms and many industries. Nevertheless, a vast industrial utilization has led to high concentrations of phosphorus in the discharge waters to the environment. The release of large phosphorus content into the natural water bodies causes major environmental concerns including eutrophication. Phosphorus and dissolved organic matters also often co-exist in wastewater [4]. The simultaneous presence of phosphorus and organic matter in such water can disturb the removal efficiency of the treatment plant due to competing effects, for example during the chemical treatment. Therefore, exploring the simultaneous removal of phosphorus and organic matter is of high importance for the optimization of the treatment process.

Coagulation and adsorption are the commonly used methods to remove NOM and phosphorus [5, 6]. However, often conventional coagulation fails to reach high removal percentages of NOM [5]. Thus, the adsorption process is attractive, as a tertiary treatment step, due to enabling efficient removal of various pollutants and the possibility of adsorbent regeneration/reuse. When adsorption is applied in the water treatment process, the activated carbon (AC) is usually used as an adsorbent. The major reasons which limit AC application in NOM removal are the high cost and high environmental impact of AC during production and transportation. Therefore, there is an urgent need to develop such efficient products from locally-globally available and eco-friendly sustainable resources to lower the carbon footprint of AC implementation in water treatment utilities.
A promising adsorbent that can substitute imported AC is biochar, which is produced through thermal conversion of biomass under limited oxygen conditions. Unlike AC, biochars are produced only from bio-based resources. The production of biochars from locally available biomass such as forestry products, algae, and agricultural wastes increases the accessibility of this bio-product worldwide. Recent research in biochar development and application for environmental remedies is a call for such environmental solutions with more advanced features for real-world applicability [7,8]. As a reusable material, biochar can be used for resource recovery or act as a fertilizer after water treatment use [9,10]. Biochar properties can be tailored via modification and changing production conditions [11]. The tailoring process of the biochars is a search for the most suitable of production conditions, which would allow producing the most efficient material, depending on the purpose [12,13]. We previously developed highly mesoporous biochars from pinecone-forestry byproduct [1,14]. The research showed that process condition and modification play a key role in tailoring the porous structure and functionality of biochars for the efficient removal of NOM from lake water. With a proper tailoring process, targeted for specific pollutants, we can maximize biochar’s performance with better results compared to that of commercial AC [14]. Biochars showed a very good performance on the simultaneous adsorption of multiple pollutants, e.g. metals [15]. On the other hand, a major challenge associated with traditional AC and biochars is a lack of selectivity [16]. The inability of biochars to selective adsorption causes a rapid loss of adsorption capacity for the target pollutant due to the adsorption of competing compounds. This challenge can be addressed by tailoring selective biochars. At the moment selective carbon adsorbents show a knowledge gap and lack of sufficient understanding as it is not well researched. Our study attempts to decrease this gap.

As such, we aimed to tailor selective biochars from forest-based biomass for the simultaneous removal of NOM and phosphorus from lake water. Spruce softwood was selected due to its large availability as a local wood species and highly porous structure that benefits the development of a porous adsorbent. The tailoring process included the impregnation of transition metals such as copper (Cu) and iron (Fe) into the porous carbonous structure, which enables a selective functionality for NOM or phosphorus. The selection of these metals for tailoring was done due to the comparison of a well-studied metal impregnated adsorbent (Fe-MIB) and a more novel adsorbent (Cu-MIB), that, as far as we know, has not been studied before for water treatment purposes. To the best of our knowledge, while recent literature reports plenty of information about the iron-impregnated biochar [17–21], there is a scarcity of knowledge on developing selective biochars through chemical activation utilizing copper salt as an activator.

Besides that, based on the previous research it was decided to produce biochars via two-step pyrolysis as the most efficient method of production [1]. Pyrolysis temperature plays a key role in the final properties of the developed biochars [22]. However, this temperature has been rarely optimized for the two-step pyrolysis method in the literature. Thus, this research aims (i) to perform chemical modification and compare common Fe-based activator and newer Cu-based activator (ii) to find the most suitable operational parameters for the production of selective adsorbents and (iii) to test the tailored biochars in selective removal of target pollutants from the lake water samples, contaminated with phosphorus and organic matter.

2. Experimental

2.1. Materials

Spruce sawdust was ordered from the Swedish University of Agricultural Sciences, Umea, Sweden, where it was prepared and sieved through a 1 mm sieve. The sawdust was stored in closed packages in a cold room before pyrolysis. Modification chemicals included FeCl₃·6H₂O (Merck) and CuCl₂·2H₂O (Sigma Aldrich). The reagents for the preparation of synthetic water solution were KH₂PO₄ (Merck) and humic acid sodium salt powder (Alfa Aesar). Lake water samples were collected from Lake Paijanne in Asikkala, Finland. To determine the chemical oxygen demand (COD) calibration curve, the used chemicals included sulfuric acid, potassium permanganate, potassium iodide, starch indicator, and sodium thiosulfate.

| Activator | 1st step T, °C | 2nd step T, °C |
|-----------|---------------|---------------|
| FeCl₃     | 200           | F11           |
|           | 250           | F21           |
|           | 300           | F31           |
| CuCl₂     | 200           | C11           |
|           | 250           | C21           |
|           | 300           | C31           |

2.2. Tailoring of biochar

Eighteen different types of metal-impregnated biochars (MIB) were tailored via two-step pyrolysis with the chemical activation process, reported in our previous research [1,14], but with different activators and pyrolysis temperature. Firstly, sawdust was pyrolyzed at three different temperatures: 200, 250, and 300 °C for 15 min under nitrogen atmosphere in Naber N60/HR furnace. Then, biochars were modified with CuCl₂ and FeCl₃. The first-step pyrolyzed biochars were mixed with chemical solutions in a 1/2 ratio of biochar/activator for 2 h in room temperature conditions. After that, they were dried for 24 h under 105 °C and finally pyrolyzed again under the nitrogen atmosphere at high temperatures 600, 700, and 800 °C resulting in MIBs. Additionally, two samples of reference biochars (RBC) were produced for comparison with tailored biochars. The lowest observed production temperatures were chosen for comparison as commonly slow pyrolysis temperatures rarely reach 600 °C [22]. For the low pyrolysis step temperature 200 °C (R200) was used and for the high pyrolysis step 600 °C (R600) without the chemical activation. After preparation, all products were rinsed with 0.1 M HCl and reverse osmosis water (RO-water) until a neutral pH was obtained and then dried at 105 °C overnight. All samples were stored at room temperature for further characterization and adsorption steps. Generally, MIBs are divided into iron-impregnated biochars (Fe-MIB) and copper-impregnated biochars (Cu-MIB). The naming of the MIB samples is tabulated in Table 1. The letters F for iron impregnation and C for copper impregnation are connected with numbers that refer to three different temperatures in the first step of pyrolysis, and three different temperatures in the second step of pyrolysis. For instance, Fe-MIB produced at 300 °C first step pyrolysis and 700 °C second step pyrolysis is named as F32 and for Cu-MIB at the same temperatures is named as C32.

2.3. Characterization of biochar

To study the functional properties of the MIBs such as morphology, composition, and porosity, the samples were characterized via scanning electron microscopy (SEM) accompanied with energy dispersive X-ray (EDX) analysis, Brunauer, Emmett and Teller (BET) specific surface area/porosity, Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD).

The SEM-EDX analysis was performed on the JEOL JSM-7500FA analytical field emission scanning electron microscope using 10 µA probe current and 10 kV acceleration voltage, to explore the surface morphology and elemental content of the samples. To prepare the sample, MIB was fixed on a metal stub with carbon tape. The coating was not performed.

The FTIR analysis was performed on PerkinElmer Spectrum Two FT-
IR Spectrometer. The spectra were recorded at room temperature within the range of 500–4000 cm\(^{-1}\) under four repetitious scans with 4 cm\(^{-1}\) resolution.

The XRD measurement was performed on a Rigaku SmartLab X-ray diffractometer to determine the crystalline structure of the MIBs. The collected patterns were analyzed, and the peaks were identified using Malvern Panalytical HighScore Plus software.

Before BET measurement samples were dried overnight and were put in Micromeritics FlowPrep 060 sample preparation system for degasification under 200 °C for 3 h with flowing N\(_2\) gas. The BET measurement was done in the Micromeritics TriStar II 3020 automated gas adsorption analyzer.

The pH drift method was employed to determine the point of zero charge (pH\(_{\text{PZC}}\)) of the MIBs [23]. The prepared series of NaCl solutions (0.1 M) pH were adjusted using NaOH (0.1 M) and HCl (0.1 M) within the range of 2–10. A known amount of the MIBs was added to the solutions and allowed to equilibrate for 24 h. The final pH of solutions was then measured and compared with the initial pH values. The pH\(_{\text{PZC}}\) was noted as the point where the final pH and initial pH were equal.

2.4. Batch experiments

2.4.1. Adsorption process

Adsorption batch experiments were conducted to study the target pollutant removal by the MIBs. The experiments were divided into three parts: (i) separate adsorption of NOM, (ii) separate adsorption of phosphorus, and (iii) simultaneous adsorption of NOM and phosphorus.

The collected lake water had a very low concentration of NOM (CODMn = 6.5 mg/l) and phosphorus (less than 0.005 mg/l) (see Table S1 in the Supplementary Information). Thus, to model the pollution, the solutions for NOM adsorption and simultaneous adsorption were prepared by adding a certain amount of humic acid sodium salt to the lake water. A stock solution of phosphorus with 1000 mg/l concentration was prepared by weighing an accurate amount of potassium dihydrogen phosphate (KH\(_2\)PO\(_4\)) and dissolving it in RO-water. Different dilutions were prepared daily before each phosphorus adsorption set. During the simultaneous adsorption test, to keep a fairly constant amount of NOM in the solution, humic acid sodium salt powder was added to the lake water and then different concentrations of KH\(_2\)PO\(_4\) were added to the solution.

A certain amount of the MIB was used for the adsorption batch experiments in a 50 ml volume of the model solution. Mixing was conducted on a shaker at 180 rpm and room temperature for 3 h until the balance was achieved according to our previous research [1]. After the 3 h contact time, the solutions were filtered through 0.45 μm syringe filters for further measurement. The removal efficiency was tested with different MIBs in the solution of a constant amount of humic acid sodium salt with 5, 10, and 20 mg/l of phosphorus. The adsorbent dosage was optimized within the 0.1–2 g/l range. The effect of pH was investigated by adjusting the solution pH at values 2, 4, 6, and 8 using HCl and NaOH.

Fig. 1. SEM images of a) RBC R200, b) RBC R600, c) Fe-MIB (sample F13), d) Cu-MIB (sample C11); and EDX analyses of e) Fe-MIB (sample F13), f) Cu-MIB (sample C11).
The batch experiments were conducted in two replicates.

2.4.2. Analytical measurements

The concentration of NOM was estimated via UV absorbance measurement at 254 nm wavelength, using a UV-VIS spectrophotometer (Shimadzu UV-1201). The samples were filtered before the measurement through 0.45 μm syringe filters. The absorbance was converted to concentration using the calibration curve of chemical oxygen demand (CODMn).

To prepare the calibration curve, a known amount of humic acid sodium salt powder was added to the RO-water. Different dilution samples were acidified with 4 M H₂SO₄. Then, KMnO₄ was added to the samples with further boiling for 20 min. After the oxidizing matter in the samples reduced part of the permanganate, the unreduced portion of permanganate was measured by the iodometric titration and collected data was used for CODMn calculation.

The phosphorus concentration in the filtrate after adsorption was measured with Discrete analyzer Skalar BlueVision, using method PO₄low: 5–500 μg/l P and method PO₄high: 0.5–5 mg/l P, in compliance with ISO 15923-1.

The percent of pollutant removal efficiency from the solution was calculated via the equation:

\[
\text{% removal} = \left(\frac{C_0 - C_1}{C_0}\right) \times 100
\]

where \(C_0\) is the initial concentration of the solution, \(C_1\) is the final concentration after adsorption.

3. Results and discussion

3.1. Material characterization

3.1.1. Morphology and composition

The surface morphology of biochars after the first step of pyrolysis R200 (Fig. 1a), the second step of pyrolysis R600 (Fig. 1b), and MIBs (Fig. 1c and d) were studied via scanning electron microscopy. Comparing Fig. 1a and b, it is seen that biochar produced at higher temperatures has a more diverse and structured surface structure than the one prepared at low temperatures. The surface morphology of the MIBs, showed an enhanced heterogeneous and porous structure with crystalline particles of ferric oxide (Fig. 1c) and copper oxide (Fig. 1d) densely covering the surface of the pores. These crystals prove the successive impregnation of metals on the surface of biochar. Successive
Impregnation of metal oxides also was proven by the EDS analysis, presented in Fig. 1e and f, and in Table 2. From the EDS analysis, it can be seen that Cl is not present in the sample, which was impregnated with FeCl₃ so iron completely transformed in oxide form, but for CuCl₂-impregnated sample it has mainly transformed to CuO (59%). However, there is still some small fraction of Cl (3.6%) untransformed in the product.

3.1.2. Functional groups

The FT-IR spectra of the RBC (R200) and MIBs showed several significant bands, illustrated in Fig. 2a. The bands at 3500–3300 cm⁻¹ correspond to O–H stretching, at 2980 cm⁻¹ and 2880 cm⁻¹ indicate asymmetric and symmetric C–H, at 2150 cm⁻¹ show C≡C, at 1640 cm⁻¹ are related to C–C stretching, at 1260 cm⁻¹ for C–O stretching, and at 1020 cm⁻¹ indicate C–H out-of-plane bending (e.g. aromatic structure of lignin) [24,25]. The peak at 620 cm⁻¹ verifies EDS results by showing the C–Cl band for Cu-MIB. Additionally, the numerous peaks in the range 1720-1260 cm⁻¹ for different aromatic compounds, which are reduced or disappeared after the activation process and thermal treatment, confirming the gasification and conversion to the graphitic structure. The disappearance of O–H stretching vibration bands for both chars suggests the oxygen in the initial materials was removed during fabrication and phenolic-aromatic structures were cracked to leave carbon solids [25]. Similar results have been reported on pinewood biochar [24].

3.1.3. XRD crystallinity

To investigate the phase transformation of metal salts during the activation and the formation of metal oxide crystals, the XRD measurements were performed on the MIBs. Fig. 2b and c shows the XRD patterns of Cu-MIB and Fe-MIB respectively. In Fig. 2b peaks match with patterns of Cu₂O located at 36.2°, 42.2°, 56.1° and CuCl at 28.4°, 47.3°, 56.1° and Cu at 43.2°, 50.3°. As clearly seen in Fig. 2c, strong diffraction peaks are located at 26.3°, 43.2°, 44.6° corresponding to carbon, and 30.3°, 35.6°, 57.2° characteristic peaks matching well with the diffraction patterns of Fe₃O₄ and/or Fe₂O₃. The detailed peak analyses obtained from HighScore Plus software can be found in Figures S1, S2, and Tables S2, S3 in the Supplementary Information.

3.1.4. BET surface area and porosity

Table 3 compiles the BET surface area, pore volume, and pore size of the RBC (R600) and MIBs. The RBC showed the highest surface area 571 m²/g, while Fe-MIB and Cu-MIB indicated 99 and 92 m²/g surface area values respectively. The decreased surface area of the MIBs confirms a successful impregnation process filling up the pores present in the carbon structure. Surface area and high porosity play a key role in the metal impregnation process. The porous structure of the biochar acts as a host for the metal oxide particles which further contribute to complexation with specific pollutants. A decreased surface area after iron impregnation was also reported previously on wood-derived biochars [19,26,27]. Therefore, the surface area around 100 m²/g is acceptable compared to many noncarbon low-cost adsorbents, such as montmorillonite [28] or bentonite [29]. However, surface area might not play a key role

### Table 3

| Sample | Surface area, m²/g | Pore volume cm³/g | Pore size, nm |
|--------|--------------------|--------------------|--------------|
| R600   | 571.2              | 0.38               | 2.7          |
| F13    | 98.9               | 0.31               | 12.4         |
| C11    | 92.4               | 0.09               | 4.1          |

![Fig. 3. Phosphorus (P) adsorption removal versus the concentration (dosage 1 g/l, contact time 3 h, no pH adjustment) a) with Fe-MIB, b) with Cu-MIB; Response surface of phosphorus removal (initial concentration 10 mg/l, T₁ – first step pyrolysis temperature, T₂ – second step pyrolysis temperature) c) with Fe-MIB, d) with Cu-MIB.](image)
regarding the adsorption of the target pollutants when compared to the role of active functional sites in the adsorption [17,30]. Analogously to the surface area, pore volume decreased from 0.38 cm$^3$/g to 0.31 and 0.09 cm$^3$/g for Fe-MIB and Cu-MIB respectively. Moreover, we can tell that copper crystals occupy much more volume than ferric ones. The pore size, on the other hand, increased from 2.7 nm to 12.4 and 4.1 nm for Fe-MIB and Cu-MIB respectively. Even though all studied biochars are considered mesoporous adsorbents (2–50 nm), the noticeable difference in pore size tells us that metal particles change the pore morphology of pristine biochar closer to the macro scale. The graphs of pore size distribution can be found in Figures S3-S5 in the Supplementary Information.

3.2. Adsorption studies

3.2.1. Determination of best-performing MIB

All MIB samples showed high phosphorus removal efficiency, which is seen in Fig. 3a and b. Sample F13, Fe-MIB in Table 1, showed the highest phosphorus removal (92% removal at lower concentration and 74% removal at higher concentration respectively). Cu-MIB C11 removed 100% of phosphorus at low concentration and 64% at high concentration.

For the identification of optimal parameters for adsorption, the response surface modeling was performed based on the obtained adsorption data, which is illustrated in Fig. 3c and d. It is seen that activation with different metals affects adsorption in a very different way at different temperatures. For Fe-MIB, the best optimal temperature appears low temperature for the first step pyrolysis and high temperature for the second step pyrolysis. The reason for that can be an active carbonyl and carboxyl functional group formation during the decomposition of wood extractives, lignin, and cellulose, which is left untouched after the first step of pyrolysis [31]. The Cu-MIB shows the best performance at low temperatures during the first step and low temperatures during the second step of pyrolysis, while the adsorption ability decreases with the temperature increase. Such phenomenon can be explained in a way that during the second step of pyrolysis, the temperature around 600 °C is suitable for lignin conversion [32], and impregnated copper salt under nitrogen gas atmosphere can bind with lignin derivatives, consequently producing complexes on the surface of the biochar. With the increase of pyrolysis temperature, these complexes start to disintegrate, which causes a reduction in the number of functional groups on the biochar surface.

Thus, the optimal parameters for MIB preparation were determined as 200 °C first step pyrolysis, 800 °C second step pyrolysis for Fe-MIB, and 200 °C first step pyrolysis, 600 °C second step pyrolysis for Cu-MIB. Therefore, to save time and resources, these two best-performing compositions were selected to produce biochars for further characterization and analysis. The chosen MIBs F13 and C11, with approximately similar adsorption ability, were characterized via numerous characterization methods reported in the previous section.

3.2.2. Effect of pH

The effect of pH on the adsorption of phosphorus was tested within the 2–8 pH range. The pH of the solution can influence the surface charge of the MIB as well as the natural state of existence of phosphorus in an aqueous medium. At lower acidic pH values, e.g. 2, phosphorus exists mainly as H$_3$PO$_4$ and H$_2$PO$_4^-$ forms. At pH 6, H$_2$PO$_4^-$ is the major phosphate species and as the initial pH of the solution increases to 9, phosphate in solution mainly exists as HPO$_4^{2-}$ and PO$_4^{3-}$ [33].

The binding of phosphate oxyanions to the adsorbent occurred more efficiently in an acidic medium, as shown in Fig. 4a. The removal of phosphorus with both MIBs generally decreased upon increasing pH. Complete removal (100%) was achieved with both F13 and C11 MIBs at pH 2, while this amount decreased to 24% and 59% of removal respectively at pH 8. This change of the removal percentage is consistent with previous studies of phosphorus adsorption on metal-functionalized bio-sorbents [34]. Even though both MIBs showed great performance in removing phosphorus at low pH values, the dependency on acidic pH for a higher removal was observed to be stronger for Fe-MIB compared to that of Cu-MIB. This suggests that Cu-MIB is less sensitive to the pH of
the solution which is also confirmed by the pHpc. At higher pH values (6–8) the surface of Fe-MIB gets negatively charged, while the Cu-MIB remains neutral and consequently can attract negatively charged molecules.

The enhanced adsorption at lower pH can be caused by the protonation of the surface functional groups of MIBs, resulting in higher phosphorus uptake due to the electrostatic attraction. The decrease in the phosphorus adsorption onto MIB by shifting pH from acidic to basic conditions can be attributed to the decrease in surface protonation of the adsorbent as well as the hydroxyl ions competition with phosphate ions for adsorptive sites [33,34]. The point of zero charge (pHPC) was identified around pH 6 for both MIB samples, resulting in a neutral surface of the adsorbent (Fig. 4a). Below pHPC, at lower pH, the surface is positively charged, partly due to the donor/acceptor interactions between the MIB structure and the hydronium ions. At pH 5–6, the surface of the MIB is neutral, the anions of phosphate can move to the surface and chelate with the Fe(III) and Cu(II) active sites. As pH increases from 6 to 8, the competitive adsorption of hydroxyl ions with phosphate ions in solution causes a visible decrease in uptake of phosphorus on the F13 MIB surface. The repelling effect on the negatively charged phosphate ions is noticed to be less for the case of C11 MIB which results in its higher removal capacity at these pH values.

3.2.3. Optimization of adsorbent dosage

The effect of MIB dosages on the removal of NOM and phosphorus is illustrated in Fig. 4b and c respectively. Both types of MIBs showed no removal for NOM at 0.1 g/l dosage. An increase in dosage from 0.1 g/l to 0.5 g/l did not affect NOM removal by MIB F13, while C11 showed a remarkable increase in removal ability to 87%. Further increase in C11 dose to 2 g/l showed a little influence on the removal. F13 also reached an increase in removal performance from 15% at 1 g/l to 97% at 2 g/l. These results indicate the higher affinity of Cu-MIB for NOM requiring a lower amount of the adsorbent compared to that of Fe-MIB. Regarding phosphorus removal, which is presented in Fig. 4c, the C11 showed a steady increase in removal percentage with the increase of the dose. Low removal (5%) at 0.1 g/l, gradually increased to 26% at 0.5 g/l, and significantly raised to 93% at 2 g/l. F13 showed an increase in adsorption with the increase of the dose until 1 g/l. With 0.1 g/l, F13 showed a 23% removal, while with 1 g/l, the removal percentage of F13 raised to 95%. With 2 g/l the removal slightly decreased to 92%. This indicates that the optimal F13 dosage for phosphorus removal is 1 g/l and a further increase is not required. The gradual improvement of adsorption by dosage is due to the access number of the exchangeable adsorptive sites on the biochar surface. The highest removal (92%) at 1 g/l by the F13 sample was the same as for C11 (93%) at 2 g/l. This suggests a better phosphorus removal performance for Fe-MIB compared to that of Cu-MIB.

3.2.4. Simultaneous adsorption

Although NOM is a complex network of molecules with different sizes and structures, the exact composition cannot be specified [35], thus its concentration is measured with a collective parameter, such as COD, representing NOM as one pollutant. Fig. 5a and b depict simultaneous removal of NOM and phosphorus, which is the variation of adsorbed amounts (mg/g) versus initial concentrations (mg/l) of phosphorus. As it is seen, for the simultaneous removal of the co-existing compounds in the water, the MIBs show different selectivity. In the case of NOM (Fig. 5a), C11 shows stable removal within the 80–90% range, which is not affected by the increasing co-existing phosphorus concentration in the water. On the other hand, the NOM removal capacity of F13 decreases dramatically from 90% to 7%, when the concentration of phosphorus increase to more than 5 mg/l. The removal of phosphorus (Fig. 5b) shows almost the opposite results. The F13 shows higher removal compared to C11 in all concentrations when NOM is present in the solution. When no NOM is added to the solution, C11 shows complete removal of phosphorus, but after the addition of NOM, the removal decreases to 85%. With a further increase of phosphorus concentration to 20 mg/l, the phosphorus removal decreases to 36%. The F13 similarly shows a decreasing phosphorus uptake with the increase of phosphorus concentration. Yet, the removal decreases from 92% at 5 mg/l without NOM to 66% at 20 mg/l of phosphorus with NOM in the solution. The RBC (R600) shows the NOM removal from 29% to 37% at 0 and 20 mg/l concentrations of co-existing phosphorus, respectively. The adsorption happens due to a relatively high BET surface (570 m²/g) enabling the NOM to reach the pores following the pore-filling mechanism. However, the RBC fails in phosphorus adsorption in simultaneous adsorption of NOM and phosphorus, as no functional groups are present on the biochar surface and no bonds could form in the competitive media.

As can be seen from Fig. 5, the RBC (having a much higher BET surface area) is unable to compete with the MIBs in the removal of the target pollutants. This supports our hypothesis that surface area is not a key factor in the adsorption performance of the target pollutants by the MIBs when compared to the importance of surface functionality. To achieve valuable and selective adsorption performance for a specific pollutant, the adsorbent needs to have suitable functional groups for the complexation of the pollutants on the surface of the adsorbent.

3.2.5. Mechanism of removal

The identification of the underlying mechanisms for the adsorption process is needed for evaluating the removal efficiency of the contaminants by the MIBs. The adsorption behavior of MIB for different contaminants is different and well correlated with the properties of contaminants. The adsorption mechanism also depends on surface functional groups, specific surface area, porous structure, and material composition.

The usual mechanisms involved in NOM adsorption on biochar are
pore filling, π–π interactions, polar/electrostatic interactions, hydrophobic effect, and hydrogen bonding [1,7,36,37]. The BET analysis confirmed that metal impregnation consumes the surface area and fills the pores of the MIB with metal oxide particles, which resulted in a relatively smaller surface area of the MIB compared to that of the RBC. Therefore, the pore-filling may not be the dominant mechanism of NOM/phosphorus adsorption on the developed adsorbents, yet the porosity of the material serves as available surface sites for functional group implementation (Fig. 6). After metal impregnation, target pollutants are attracted to the certain functional groups entrenched in the MIB structure, affecting the selectivity of the material. Thus, the NOM molecules undergo ligand complexation with positively charged copper sites, which are the active functional groups provided by the Cu-MIB. Phosphorus, on the other hand, has an affinity towards iron and undergoes chemisorption with iron-based active sites on the Fe-MIB surface, showing selective phosphorus adsorption. The iron modification introduces functional sites on carbon structure, which can provide the chemical co-precipitation of Fe$^{3+}$/Fe$^{2+}$, expressed as follows [38]:

$$\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}$$

(2)

In this process, the biochar surface promotes the nucleation of iron oxide precipitation. Crystalline Fe$_3$O$_4$ and Fe$_2$O$_3$ particles form within the Fe-MIB porous structure, as was confirmed by XRD analysis. Therefore, adsorption capacity is due to the iron oxide-containing groups that exist in the Fe-MIB.

4. Conclusions

The tailoring process of MIB was optimized by comparing the influence of pyrolysis temperature and two different activators during the production stage. The NOM was selectively adsorbed from the binary solution by the Cu-MIB and phosphorus was selectively removed by the Fe-MIB. Adsorption results, along with the characterization, confirm that the metal oxide contents within the porous structure of MIB play the role of active sites for the selective removal of target pollutants. This study points towards the tailoring process of biochars for more specialized applications such as selective removal of specific pollutants from the water phase.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.micromeso.2021.111499.

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