Sustainable synthesis of rose flower-like magnetic biochar from tea waste for environmental applications

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Introduction: Biochar utilization for adsorption seems to be the most cost-effective, easy/fast approach for pollutants removal from water and wastewater. Due to the high adsorption properties, magnetic biochar proved to be efficient in the sorption of heavy metals and nutrients. Although there are several studies on development of magnetic biochars, there is a lack of research on development of high-performance magnetic biochar from food waste for removal applications.

Objectives: This study aimed at preparing new classes of magnetic biochar derived from tea waste (TBC) for removal of heavy metals (Ni2+, Co2+), and nutrients (NH4+ and PO43−/Co3−) from water and effective fertilizer (source of NH4+ and PO43−).

Methods: Standard carbonization process and ultrafast microwave have been used for fabrication of TBCs. The removal of nickel, cobalt as the representatives of heavy metals, and over-enriched nutrients (NH4+ and PO43−) from water were tested and the removal kinetics, mechanism, and the effect of pH, dissolved organic matter and ionic strength were studied. Simultaneously, possible fertilizing effect of TBC for controlled release of nutrients (NH4+ and PO43−) in soil was investigated.

Results: Up to 147.84 mg g−1 of Ni2+ and 160.00 mg g−1 of Co2+ were adsorbed onto tested biochars. The process of co-adsorption was also efficient (at least 131.68 mg g−1 of Co2+ and 160.00 mg g−1 of Ni2+). The highest adsorbed amount of NH4+ was 49.43 mg g−1, and the highest amount of PO43− was 112.61 mg g−1.
Introduction

The removal of pollutants from water using waste derived adsorbents has received significant attention lately [1–4]. One of the important adsorbents obtained from biomaterials is biochar. Biochar is derived from thermal decomposition of plant biomass in partial or total absence of oxygen [5–7]. Chemically, it is a char black carbon that comprises a large fraction of organic matter [1]. Biochars are widely studied due to their low cost and versatile applications [8,9] in agriculture such as improved soil fertility, water retention or crop yield [2,5,10], environmental protection applications [8,9] in agriculture such as improved soil fertility, and hinder the large-scale application of biochar as an adsorbent. The concentration of heavy metals is found to be higher in the edible parts of plant (leaves and roots). Simultaneously, the enrichment of soil in Ni than Co when irrigated by the treated wastewater was found. Due to the bioavailability and toxicity of Ni2+, Co2+, N H4+ is toxic to plants, bacteria and aquatic animals [41], whereas P is a major nutrient in soil possessing however lowest mobility and though phytoavailability [42].

Microwave assisted pyrolysis (MWAP) is an alternative heating approach to convert organic waste materials into value-added products, such as biochar (BC) that can be used widely for environmental applications. The MWAP is a sustainable, cost-effective and environmentally friendly route in development of high-performance biochar [29,30]. Microwave (MW) valorization of biomass to biofuels represents an economically viable and harmless approach by virtue of high availability of raw materials, and thermochemical process with positive energy ratio [31].

Magnetization of biochar [18,22,28,29] can be obtained by various methods including i) impregnation-pyrolysis, ii) coprecipitation, iii) reductive co-deposition or iv) hydrothermal carbonization. The literature data on magnetization effect on biochar adsorption properties are indicating that different response can be noted both increased [18] or reduced [22,32] adsorption capacity. The application of Fe during biochar production [33] have an impact on biochar properties such as the adsorption ability and selectivity resulted from the surface modification and creation of “engineered biochar”.

Heavy metals are widely recognized as pollutants [34,35]. The toxicity of nickel (Ni) and cobalt (Co) is well known [34,36]. Their concentrations must be monitored in environmental matrices. The concentrations in drinking water should not exceed: 0.005 mg L⁻¹ for cobalt [37] and 0.1 mg L⁻¹ of Ni [38]. Nickel sources include incineration, batteries and industrial and domestic wastewater e.g. production of alloys or food processing, respectively [38]. In the environment, the main accumulation tank for Co and Ni is soil. The maximum permissible level of Co and Ni in agricultural soils is as follows: 39 and 420 mg/kg dry mass (d.m.) according to US EPA, and 20–40 and 300–400 mg/kg d.m. according to EU Commission [39]. Some trace metals tend to accumulate in the crops or vegetables. The literature data [40] indicate that Ni revealed higher tendency for accumulation in radish leaves than other metals such as Cr or Co. The concentration of heavy metals is found to be higher in the edible parts of plant (leaves and roots). Simultaneously, the enrichment of soil in Ni than Co when irrigated by the treated wastewater was found. Due to the bioavailability and toxicity of Co²⁺ and Ni²⁺ there is a need to develop new methods for their removal from water.

On the other hand, the presence of some nutrients in water or wastewater such as nitrogen (N, in the form of NH₄⁺ or phosphorus (P, in the form of PO₄³⁻) is responsible for the increased problem of eutrophication [41]. Apart from [un]treated wastewater, N and P source can be lost from soil, enriched when chemical fertilizers were additionally used [41]. The high level N-NH₄⁺ is toxic to plants, bacteria and aquatic animals [41], whereas P is a major nutrient in soil possessing however lowest mobility and though phytoavailability [42].

Adsorption seems to be the most cost effective, easy and fast method for pollutants removal [6,7,16,43]. Due to the high adsorption properties, magnetic biochar can be used for sorption of both heavy metals and nutrients from aqueous solution. Although there are several studies on heavy metal adsorption onto magnetic biochars or biochars obtained from Hot Drinks Wastes [44], to the best of our knowledge this is the first report on use of easily separable [18] rose flower-like magnetic tea waste based biochar (TBC) for Ni²⁺, Co²⁺, NH₄⁺ and PO₄³⁻ adsorption. The effect of magnetization type i) two step vs. one step carbonization, ii) microwave assisted carbonization, were tested. Additionally, the potential use of TBC as fertilizer for controlled release of nutrients in soil was estimated.

Experimental

Materials and methods

The household tea waste was used as the biochar precursor. The tea waste was washed and dried at room temperature prior to heat treatment in air at 250 °C (3hr). Three different approaches were used for magnetization process. For synthesis of the Tube furnace (TF) samples, heat treated tea wastes are firstly carbonized in argon atmosphere and then carbonized tea wastes (CTW) are subjected to the magnetization process in tube furnace. For making a microwave sample (MW), heat treated tea waste was first carbonized in tube furnace and then magnetization was performed in a microwave for 10 s using ammonium iron(II) sulphate. The last set of samples was single stage samples (SS) where the process of the carbonization of the stabilized tea waste and magnetization
were combined and performed in a tube furnace. The details of the processes are presented in Fig. 1.

For magnetization process, ammonium iron(II) sulphate (supplied by Chem-supply, X) was used. Using the thermal process, ammonium iron(II) sulphate which contains Fe(II) species is decomposed at 230 °C, and Fe(III) species appears according to the following reaction [29,30]:

\[2(NH_4)_2Fe(SO_4)_2 \rightarrow (NH_4)_2Fe_2(SO_4)_3 + (NH_4)_2SO_4\] (1)

As the presence of both iron species is required to form magnetite nanoparticles (MNPs), application of this unique double salt simplifies the complex Fe₃O₄ MNPs preparation method. H₂O molecules are formed by dehydration of the compounds and at 450 °C Fe₂(SO₄)₃ and FeSO₄ are formed by the decomposition of the salt [45,46]. During the heat treatment process, the conversion of Fe-based structure to Fe₂O₃ occurred at ~640 °C [47,48] and Fe₃O₄ nanoparticles are formed by thermal conversion of Fe₂O₃ in inert atmosphere (Nitrogen) [49]. Formation of Fe₃O₄ magnetic nanoparticles on the surface of tea waste or carbonized tea waste were carried out by immersing the CTW in an aqueous solution of ammonium iron(II) sulphate. To remove remained air in samples and accelerate the ion transfer into structure, samples are subjected to degassing process in vacuum chamber for 30 min. Surface decoration of CTW with MNPs was carried out by a very intense heating sequence in a microwave oven (LG 1100Watt) for 2 cycles of 10 s in MW samples. In case of TF and SS samples, the process of magnetization was performed in a tube furnace (10 °C min⁻¹, dwelling time (1hr) at 800 °C). The samples are tested for BET surface area using low temperature N₂ adsorption and BET method in Autosorb Quantachrome and structural imaging were performed using a Zeiss Supra TM 55VP SEM.

Sorption experiment

Sorption was monitored in the batch experiments in 40-mL Teflon centrifuge tubes. Three biochars (50 mg) and an initial 10 mg L⁻¹ concentration of Ni²⁺ and/or Co²⁺ and 50 mg L⁻¹ of NH₄⁺ or/and PO₄³⁻ were used in biocide background solution (0.01 mol L⁻¹ CaCl₂ and 3.08 mmol L⁻¹ NaN₃ in deionized distilled water). Samples were shaken in the dark (rotary shaker 200 rpm) for seven days at ambient temperature (23 ± 1 °C).

The adsorption experiments over the pH range 5–9 for NH₄⁺ and 5.8–9.15 for PO₄³⁻ and 2–6.54 for Co²⁺ and Ni²⁺ were performed to find an optimal pH. Solution pH values were adjusted with 0.1 M HCl and/or 0.1 M NaOH.

Sorption kinetics was monitored in the batch experiments in 40-mL Teflon centrifuge tubes. Biochars (50 mg) and an initial 20 µg L⁻¹ concentration of Ni²⁺, Co²⁺ and 50 mg L⁻¹ of NH₄⁺ and PO₄³⁻ were prepared in biocide background solution at pHCo = 6.4, pHNi = 6.4, pHCo+Ni = 6.4, pHNH₄⁺ = 6.60, pHPO₄³⁻ = 7.88, pHNH₄⁺+PO₄³⁻ = 7.47 being the most suitable according to the obtained results of the studies.

Samples were shaken in the dark (rotary shaker 200 rpm) at ambient temperature (23 ± 1 °C). At selected time intervals (2, 8,

![Fig. 1. Schematic diagram of developing of magnetic tea waste biochar.](image-url)
24, 48, 72 and 168 h) tubes were centrifuged (1000 g for 20 min) and the mass of adsorbed ions was determined. The adsorbed mass was calculated based on the decrease of the solute concentration in the aqueous phase. There was no measurable change in concentrations in the control vials.

For the determination of adsorption isotherms, a batch equilibration technique at 23 ± 1 °C in the dark was employed using 50 mg of TBC in the background solution and 10–100 mg L⁻¹ of tested solutions. The tubes were shaken (200 rpm) and after seven days (adsorption time necessary to obtain equilibrium obtained in preliminary studies), the tubes were centrifuged and the concentration of adsorbates in solution phase was determined by appropriate methods. Each concentration point, including blanks, was run in duplicate.

The effect of ionic strength was assessed using NaCl solutions in the range of 0–100 mM Na⁺. Simultaneously the effect of dissolved organic matter was estimated using tannic acid solutions 0–100 mg L⁻¹. In the end, the test with agricultural soil was performed using 1 g of tops soil samples (0–20 cm) from Lublin area (Poland), previously dried at 40 °C and sieved (2 mm). To soil a TBC (50 mg) and 40 mL of NH₄⁺ + PO₄³⁻ solution (50 mg L⁻¹ each) were added. The samples were covered in aluminum foil and shaken (200 rpm) for 6 days. The amount of NH₄⁺ + PO₄³⁻ was estimated in supernatant after centrifugation.

Ions and data analysis

The voltammetric measurements of Co²⁺ and Ni²⁺ were performed using mAUTOLAB analyzer (Eco Chemie, The Netherlands) controlled by GPES 4.9 software in a 10 mL electrochemical cell with a lead film glassy carbon electrode (PbF/GCE) as a working electrode, Pt wire and Ag/AgCl, KCl (3 mol L⁻¹) as auxiliary and reference electrodes, respectively [50].

NH₄⁺ and PO₄³⁻ ions were analyzed using the MIC 3 ion chromatographer by Metrohm. A SUPP 5 250 analytical column (eluents: sodium bicarbonate/sodium carbonate concentrate - Sigma Aldrich, flow rate 0.7 mL min⁻¹) and a Metrosep C4 150 analytical column (eluents: Nitric acid/Dipicolinic acid concentrate - Sigma Aldrich, flow rate 0.9 mL min⁻¹) were applied for anions and cations analysis, respectively. Conductometric detection for both cation and anion analysis was conducted [51,52].

For the description of Co²⁺, Ni²⁺, NH₄⁺ and PO₄³⁻ adsorption four kinetic models: pseudo first (PFO), pseudo-second order (PSO), Elovich and Intraparticle diffusion model (IPD) were applied. Langmuir (L), Freundlich (F), Temkin (T) and Dubinin-Radushkevich (DR) models were used for the testing of the adsorption isotherms. Detailed information about the models, kinetic curves, and isotherm fitting are presented in the Supporting Information (Table S1).

Results and discussion

Structural and surface properties

The details of the BET results and surface properties of the TBC are included in Table 1. As clearly seen, sample SS showed the highest surface area, while MW sample exhibited the lowest surface area. Except the MW sample, TF and SS samples showed acceptable surface area in the category of carbonized biochar for removal applications. SS sample showed higher surface area than activated tea waste in H₂SO₄ [53]. In case of pore diameter, sample TF showed a very small pores size (1.5 nm) compared to 3.93 and 4.17 nm for SS and MW samples, respectively. This is in agreement with the pore volume of the samples that showed the highest for TF sample compared to SS and MW samples. It is evident that a

| Sample | Surface Area(m²/g) | Pore Volume (cc/g) | Pore Diameter (nm) |
|--------|--------------------|--------------------|--------------------|
| MW     | 41.259             | 0.077              | 4.175              |
| SS     | 184.460            | 0.084              | 3.933              |
| TF     | 111.215            | 0.201              | 1.5656             |

Fig. 2. Isothermal absorption/desorption patterns (a, b, c) and Pore size distribution (d-i) of different tea biochar.
large number of small pores and a small number of large pores are seen for sample TF. In case of MW and SS samples, they showed a broad range of pore size ranging from 4 nm to more than 10 nm (see Fig. 2).

SEM micrographs of the CTW and TF sample are shown in Fig. 3. The rose flower like pattern of CTW with a central void is observed for all samples. After the magnetization, the nanoparticles that absorbed onto the surface, have been converted into the Fe$_3$O$_4$.
magnetic nanoparticles and distributed on the surface homogeneously. As can be seen some areas seems to be more attractive for adhesion of nanoparticles due to lower surface energy such as the void in the center of the rose flower (see Fig. 3H). It is observed that there are numerous macroscopic pores and nanopores in particular in the void area of the rose flower which may be due to the release of gases from the core towards the outer surface of precursor and also carbonization and removal of non-carbon atoms in forms of water and oxides of nitrogen and carbon from the material [53]. It can be concluded that carbonization and magnetization process resulted in the development of porous structure in tea waste based biochar.

FT-IR spectra presented in Fig. 4 indicate that the surface of TBC was enriched in surface functionalities. TW before (Fig. 4A), both raw and stabilized and after carbonization were possessing several surface functional groups. Bands at ~2900 and 2840 cm$^{-1}$ were confirming the presence of CH$_3$ groups both in aromatic rings and alkanes (C-H stretching) resulting from the presence of lignin and holocellulose [33].

The characteristic peaks at 3400–3300 cm$^{-1}$, 3188 cm$^{-1}$, 2842 cm$^{-1}$, 1651 cm$^{-1}$, 1518 cm$^{-1}$, 1047 cm$^{-1}$ and 852 cm$^{-1}$ were responsible for stretching of N–H, =C–H sp$^2$, C–H for methyl, C=O, aromatic C=C, alcoholic C–O and C–O–C and out-of-plan aromatic C–H bending vibrations, respectively [54].

Fig. 4C and D represents results of Raman spectroscopy analysis on tea wastes biochars, before and after magnetization. Since the stabilized and carbonized Tea wastes will be subjected to a harsh MNPs growth reaction, study of graphitic structure of the CMT substrate provide the idea of the how the microwave assisted MNPs formation reaction is working. As a rule, the higher graphite content of carbonaceous materials enhances the joule heating mechanism and results in the higher microwave absorption at the same reaction condition [17,55–58]. Based on the presented Raman spectra in Fig. 3A, the MNP characteristic peak is observed when the laser spotted at an accumulation of nanoparticles. After microwave assisted magnetization, the ID/IG ratio and a substantial growth in the ratio was observed in comparison to STW and CTW samples. The higher disordered ratio in magnetized samples
is due to the higher microwave absorption of TBCs and related to the size of graphite crystallites.

**Adsorption studies**

In order to evaluate the releases of readily soluble ions from TBC, they were extracted by cold DI water. Results of the readily soluble ions are presented in Table 2.

It can be seen that the obtained biochar differ in content of soluble ions. Highest initial content of PO$_4^{3-}$/C$_0$ was noted in SS sample, and NH$_4^+$ in MW sample. The highest pH was obtained for TF and SS samples. Increased pH may imply the presence of inorganic alkaline components in the biochars [59].

**pH effect**

In the first stage of the adsorption study the most preferential adsorption conditions for all tested ions and TBC were selected (Fig. 5). pH have an effect on the adsorbent’s surface charge, the degree of ionization and the speciation of adsorbates [40]. The obtained data clearly indicate that the optimum pH conditions for adsorption onto MW TBC are: Ni – 6, Co – 2 (however at pH = 6, 81% of Cs in strong acid conditions were noted), NH$_4^+$ – 7.14, PO$_4^{3-}$ – 7.2), SS: Ni – 4, Co – above 5.6, NH$_4^+$ – 6–9, PO$_4^{3-}$ – 9; TF: Ni – 6, Co – 5, NH$_4^+$ – 9, PO$_4^{3-}$ – 7.2.

At low pH, the competition between NH$_4^+$ and H$^+$ was responsible for lower adsorption, similarly to the competitive effect of NH$_4^+$ and OH$^-$ reaction in the solution at higher pH values [60] or created at high pH NH$_3$ + H$_2$O, is less favorable for ion exchange [41].

Generally, at higher pH values, the precipitation of metal hydroxides is observed. For Ni the pH of precipitation is 10–11, whereas for Co it starts at 6.9 [61], though the tests were performed up to pH = 7 for Ni and Co adsorption. The observed increase of C$_0$ of Ni or Co with increased pH was connected with the fact that at lower pH values, the concentration of H$^+$ was very high competing with metal cations and the ion exchange site onto TBC hindering adsorption. At higher pH values, lower concentration of H$^+$ was noted and higher adsorption of Ni or Co, occurred via the ion exchange [62]. Under acidic conditions in the environment the mobility of Ni is increased implying the enhanced availability. As the noted effect was not strictly linear, the adsorption studies were further conducted without pH adjustments based on initial concentration of applied salt.

Adsorption of NH$_4^+$ or PO$_4^{3-}$ affected pH noted at the end of the process. Although TF sample possessed highest pH, adsorption of NH$_4^+$ lowered this value much more than in case of SS sample. During NH$_4^+$ adsorption, SS surface properties were changed in the highest extend. Acidic surface of MW during PO$_4^{3-}$ adsorption possessed the lowest pH after adsorption. Typically, the surface of biochars can be negatively charged and application of magnetization affected surface charge [18] and the observed effect was strictly connected with magnetization process type. Microwave magnetization was connected with creation of the most acidic surface among tested TBC, that was confirmed by FT-IR studies (=CO, –COO functional groups).

Generally, at pH 2–7 H$_2$PO$_4^-$ is dominating whereas HPO$_4^{2-}$ is most abundant when pH is 7–12, and at pH 4–10 phosphate existed in both forms of HPO$_4^{2-}$ and H$_2$PO$_4^-$ in solution affecting surface electrostatic interactions between phosphate ions and TBC negatively charged surface resulting in low PO$_4^{3-}$ adsorption in comparison to other adsorbates. Surface of TF and SS during PO$_4^{3-}$ adsorption was not prone to pH changes. However, at very high pH values (>10) increased electrostatic repulsions between the negative surface of TBC and the increasingly multivalent P oxyanions (pK$_{a2}$ = 7.21, pK$_{a3}$ = 12.67) can be observed. TBC can be applied for the removal of nutrients from water, especially that
natural eutrophic waters are characterized by pH from 7 to 9 and $P < 1 \text{ mg L}^{-1}$ [42]. Similar effect was noted in the studies of Wan et al. [62] or Cai et al. [42].

### Kinetics

In order to investigate the mechanism of adsorption and potential rate controlling steps such as mass transfer and chemical reaction process the kinetics of $\text{Ni}^{2+}$, $\text{Co}^{2+}$, $\text{Ni}^{2+} + \text{Co}^{2+}$ and $\text{NH}_4^+ + \text{PO}_4^{3-}$ adsorption was tested using four well known and widely tested kinetic models: pseudo-first order (PFO), pseudo-second order (PSO), Elovich and Intraparticle diffusion (IPD) that were described in Supplementary Information (Table S1).

The kinetic of $\text{Ni}^{2+}$ and/or $\text{Co}^{2+}$ adsorption onto TBC was presented in Fig. 6 and Table S2. It can be seen that the adsorption of $\text{Co}^{2+}$ and $\text{Ni}^{2+}$ was fast and more than 51% of $\text{Ni}^{2+}$ and $\text{Co}^{2+}$ from single solute system, and 56% and 50% from $\text{Ni}^{2+} + \text{Co}^{2+}$ mixture, respectively, was adsorbed in first 8 h. However, adsorption of $\text{Co}^{2+}$ was faster than $\text{Ni}^{2+}$. Generally, the amount of adsorbed $\text{Ni}^{2+}$ after 7 days of sorption process was similar for all TBC and $q_{\text{Ni}}$ was 144.84–147.84 mg g$^{-1}$. In the mixture it can be observed that the presence of $\text{Ni}^{2+}$ lowered $\text{Co}^{2+}$ adsorption only onto SS TBC (from 145.76 to 131.68 mg g$^{-1}$). In case of the other TBC, the obtained $q_e$ values were as high as 160 mg g$^{-1}$. This imply that SS surface is preferential to $\text{Ni}^{2+}$ and $\text{Co}^{2+}$ co-adsorption, maybe due to the highest surface area ($184.460 \text{ m}^2 \text{ g}^{-1}$) where there was enough place for adsorption of these two ions [61]. In the multi component solutions there is enough space for adsorption sites for both metals [63].

Co-adsorption of $\text{NH}_4^+$ and $\text{PO}_4^{3-}$ was not favorable onto tested TBC in comparison to $\text{Ni}^{2+}$ and/or $\text{Co}^{2+}$ (Table 3). $\text{NH}_4^+$ adsorption was fast – in first 5 h at least 65% of maximum adsorption was noted. The adsorption of $\text{PO}_4^{3-}$ onto SS and TF was lower than $\text{NH}_4^+$ after 5 h was 45% of $\text{PO}_4^{3-}$ was adsorbed. The highest amount of $\text{NH}_4^+$ was adsorbed onto SS (49.43 mg g$^{-1}$), and the highest amount of $\text{PO}_4^{3-}$ was noted onto MW (112.61 mg g$^{-1}$). These values were significantly higher than to those obtained in the studies of Wang et al. [13] (4.13 mg g$^{-1}$ $\text{NH}_4^+$ and 19.75 mg g$^{-1}$ $\text{PO}_4^{3-}$), Cai et al. [42] (2 mg g$^{-1}$P), Lu et al. (19.26454 mg g$^{-1}$ min$^{-1}$) [60] or Wan et al. (5.21 mg g$^{-1}$ for $\text{PO}_4^{3-}$ [62]) but slightly lower than Xie et al. (64.90 mg g$^{-1}$ $\text{NH}_4^+$-N [41]) or similar to Li et al. (121.25 mg g$^{-1}$P [64]).

Generally, the sorption studies indicated that over SS and TF TBC surface there were less adsorption sites for anions on the surface and $\text{PO}_4^{3-}$ have to compete with $\text{NH}_4^+$ for the free adsorption sites. It was noted in literature that biochar with relatively high alkalinity (pH 7–12) was characterized by a low anion exchange capacity (<5 cmol kg$^{-1}$) and very limited sorption capacity towards...
the negatively charged anions, such as PO$_4^{3-}$ [42]. The overall removal capacity for the different ions was as follows:

\[
\text{MW: Co}^{2+} > \text{Ni}^{2+} > \text{PO}_4^{3-} > \text{NH}_4^+ \\
\text{SS: Co}^{2+} > \text{Ni}^{2+} > \text{NH}_4^+ > \text{PO}_4^{3-} \\
\text{TF: Co}^{2+} > \text{Ni}^{2+} > \text{NH}_4^+ > \text{PO}_4^{3-}
\]

Chemisorption was the rate limiting step during adsorption Ni$^{2+}$ and Co$^{2+}$ from single solute system and mixture solution. The $R^2$ values higher than 0.997 were confirming a great fitting of experimental data of Ni$^{2+}$, Co$^{2+}$, Ni$^{2+}$+Co$^{2+}$ adsorption to the PSO model. Additionally, the calculated $q_{\text{exp}}$ in PSO were similar to the $q_e$. Interestingly, the process of NH$_4^+$ adsorption onto MW and PO$_4^{3-}$ adsorption onto SS revealed a best fitting to Elovich model. Considering the Elovich model parameters, higher value of $\alpha$ than $\beta$ indicated higher adsorption rate than desorption. PSO regime is the mostly applied for the description of adsorption of metals and nutrients onto biochars [13,41,42]. Elovich model was also describing the adsorption of tetracycline onto mesoporous tea waste derived biochar [65].

Considering the mechanism of diffusion, a good fitting of film diffusion can be observed only in case of PO$_4^{3-}$ onto all TBC, NH$_4^+$ onto SS and TF samples, Ni$^{2+}$ in Co$^{2+}$ presence onto all TBC; however, film diffusion might not be the sole rate-limiting step. In the studies of Hokkanen et al. [61], although PSO regime revealed a good fitting, higher applicability for Ni$^{2+}$ and PO$_4^{3-}$ adsorption revealed PFO.

The positive correlation between $k_2$ noted for Co$^{2+}$ adsorption and pore volume was noted ($p < 0.05$) confirming the role of pore filling mechanism and participation of pores in adsorption. However, negative correlation with pore diameter ($p < 0.001$) indicates that the pore with lower diameter were preferred for Co$^{2+}$ adsorption onto TBC. In Ni$^{2+}$ adsorption in Co$^{2+}$ presence the key point is surface area of TBC ($p < 0.1$), however, again, lower surface area was preferred in Ni$^{2+}$ adsorption. No correlation between $k_2$ during NH$_4^+$ or PO$_4^{3-}$ adsorption and TBC properties was noted.

In IPD model two phases can be observed expressed as two linear regions in IPD curve. The first fast step was connected with the spread of ions on TBC surface. $k_{\text{id1}}$ was higher usually than $k_{\text{id2}}$ indicating that the process was fast whereas low $k_{\text{id2}}$ values inform on slow process of ions adsorption [60]. Due to the fact that the intercept of linear form is not zero, then intraparticle diffusion is not a regnant mechanism and does not determine the mass transfer rate in the adsorption process [60]. If $k_{\text{id1}}$ is higher than $k_{\text{id2}}$ [66] the faster rate of film diffusion than intraparticle diffusion is considered. Interestingly, Ni$^{2+}$, Co$^{2+}$ and NH$_4^+$ adsorption onto MW was governed by intraparticle diffusion than film diffusion. It was concluded that the adsorption kinetics might be controlled by both film diffusion and intra-particle diffusion simultaneously [66].

Fig. 6. Kinetics of (A) Ni$^{2+}$, (B) Co$^{2+}$, (C) Ni$^{2+}$+Co$^{2+}$, (D) NH$_4^+$ and PO$_4^{3-}$ adsorption onto TBC.
Isotherms

The adsorption isotherms were nonlinear indicating a clear dependence of the sorption capacity from the ions concentration. Four nonlinear isotherm models (Freundlich, $F$, Langmuir, $L$, Temkin, $T$, and Dubinin-Radushkevich, $DR$) were tested to fit the experimental data. Application of $L$, $F$, $T$ or $DR$ models had the highest coefficient of determination ($R^2$) (Table S2).

$R^2$ values were as high as 0.94 indicating good fitting of experimental data to tested models; however, there were two fittings with lower $R^2$ value (0.85 and 0.74), that were describing PO$_4^{3-}$ adsorption onto MW and TF. Langmuir model indicating monolayer surface coverage onto homogeneous surfaces [67] was describing the adsorption of Ni$^{2+}$ onto MW, Co$^{2+}$ in the presence of Ni onto MW, and NH$_4^+$ onto MW, SS and TF TBC (Table S2, Fig. 7). $Q_l$ describes the monolayer coverage and represents the practical limiting adsorption capacity, whereas $K_L$ (L mg$^{-1}$), Langmuir equilibrium constant, is related to the affinity of the binding sites (the bond energy) for the adsorption reaction between metal and material [61]. The larger the $K_L$, the stronger the bond between adsorbate and adsorbent [60]. In $L$ model, the highest $Q_l$ (maximum amount adsorbed) was noted for NH$_4^+$ adsorption onto MW (1633.28 mg g$^{-1}$) indicating the highest adsorption capacity of MW towards NH$_4^+$. Simultaneously, the adsorption capacity of SS sample towards NH$_4^+$ adsorption was the lowest. $Q_l$ in PO$_4^{3-}$ adsorption onto tested TBC was negatively correlated with pore volume ($p < 0.1$) indicating that wide pores were available firstly as adsorption sites. The data included in Table S2 show that the Langmuir isotherm was favorable ($0 < R_L < 1$). Langmuir model was also applied for the description of NH$_4^+$ adsorption onto La-modified biochar produced from oak sawdust ($Q_l = 10.1$ mg g$^{-1}$) [13], PO$_4^{3-}$ adsorption onto protonated g-C$_3$N$_4$ and acid-activated montmorillonite composite [62], MgO decorated biochar [64] or organics removal over tea waste biochar [68–70].

More complicated mechanisms e.g. the surface heterogeneity or interactions between adsorbing species were noted in case of the other adsorbates and adsorbents [61]. The process of Co$^{2+}$ adsorption form single solute system was ascribed to $F$ model and multilayer adsorption. Good fitting of $F$ model was also noted in case of Ni$^{2+}$ adsorption onto SS, and Ni$^{2+}$ in Co$^{2+}$ presence onto SS. In the Freundlich model, sorption onto sites with different energy is assumed and the energy of sorption sites depends on the degree of surface coverage with adsorbate molecules and the interactions between adsorbed molecules. In $F$ model the highest value of $Q_F$ (the relative adsorption capacity) was noted for Co$^{2+}$ adsorption onto SS sample (152.127 mg g$^{-1}$). The value of $1/n$ (parameter related to linearity) is above 1 indicating unfavorable adsorption and its chemical character [53].

Adsorption of Ni$^{2+}$ onto TF, Ni$^{2+}$ in Co$^{2+}$ presence onto TF, Co$^{2+}$ in Ni$^{2+}$ presence onto SS and TF and PO$_4^{3-}$ onto MW was fitted Temkin...
model. $T$ model is considering heterogeneity of the surface. The highest $Q_T$ was noted for Ni$^{2+}$ adsorption onto TF sample – 3.350 mg g$^{-1}$. The other parameter, $B$ - heat of adsorption, can be used to distinguish physical and chemical adsorption mechanism. The highest $B$ value was noted for Ni$^{2+}$ adsorption onto TF, 26.86 J mol$^{-1}$. The conversion of $B$ values from J mol$^{-1}$ to kcal mol$^{-1}$ resulted in low values < 1 kcal mol$^{-1}$ what indicates that physical sorption was dominant.

$DR$ model can be used for the description of Ni$^{2+}$ adsorption in Co$^{2+}$ presence onto MW and PO$_4^{2-}$ onto SS or TF. The highest $Q_D$ value was noted in Ni$^{2+}$ adsorption onto TF in the presence of Co$^{2+}$ (624.05 mg g$^{-1}$). According to $DR$ model the adsorption occurs onto heterogeneous surfaces of adsorbent [71] and is related to micropores volume filling as opposed to layer-by-layer adsorption on pore walls [72]. It can be clearly seen that the addition of co-solute in case of metals changed the mechanism of adsorption, for example onto MW, where Ni$^{2+}$ was adsorbed by monolayer and after Co$^{2+}$ addition the highest impact of pore filling was revealed. The highest $Q_{DR}$ was noted for Ni$^{2+}$ adsorption in Co$^{2+}$ presence onto MW (624.05 mg g$^{-1}$). The obtained mean free energy ($E$ greater than 8 kJ mol$^{-1}$) indicated a chemisorption process. Comparison of $E$ values between metals and nutrients indicated that heavy metal ions revealed more affinity to ion-exchange process [41]. Similarly, $Q_{DR}$ values were lower than $Q_L$ what may indicate that not all micro/macropores were occupied with solute [41].
Several mechanism of adsorption of cationic heavy metals onto magnetic biochar were proposed: 1) electrostatic adsorption; 2) ion (ligand) exchange; 3) surface or inner-sphere complexation; 4) \( \pi - \pi \) interaction; 5) internal spherical complexation; 6) hydrogen bonding; 7) co-deposition [18]. All these mechanism can contribute to adsorption onto TBC [69]. However, adsorption process is affected both by the character of adsorbent (characteristics of the binding sites (e.g. functional groups, structure, surface properties, etc.), and the properties of the adsorbate (e.g. concentration, size, charge, molecular structure, pH, ionic strength, co-solvents etc.) [61]. The main surface groups onto TBC that participate in adsorption are graphite or aromatic carbon (C–C, C–H), alkoxy (C–O), carbonyl (C = O) and carboxyl (COOH) functional groups [18]. PO₄³⁻ adsorption was observed via electrostatic interaction H-bonds, whereas metal cation were adsorbed with the participation of complexation and electrostatic interaction [8].

**Ionic strength effect**

It can be clearly seen from the Fig. 8 that the increase of the solution ionic strength (IS) affected Ni²⁺ and Co²⁺ adsorption onto tested TBC: the greatest effect was noted in case of TF. In case of NH₄⁺ + PO₄³⁻ interestingly, the values of \( C_i \) were increased for NH₄⁺ adsorption onto MW and SS, and PO₄³⁻ onto TF. PO₄³⁻ adsorption onto MW seemed to be not affected by solutions ionic strength in applied concentration range (Na⁺ 25–50 mM).

The increase of IS affected both the amount of adsorbed Ni²⁺+Co²⁺ and the reaction mechanism (Table 3S). In the presence of Na⁺
the monolayer adsorption of Ni$^{2+}$ onto MW was noted. Ni$^{2+}$ adsorption onto SS was changed from multilayer (F) to T. Surprisingly, Co$^{2+}$ adsorption onto MW was directed from monolayer to multilayer formation (from L to F) indicating that more intense competition between ions and MW surface was noted [60]. Negative values of B (heat of adsorption) in T model were indicating that the adsorption process was exothermic.

**DOM effect**

Nickel in natural waters occurs predominantly as the ion Ni(H$_2$O)$_{5}$$^{2+}$ (pH 5–9) rather than in complexes with ligands, such as OH$^-$, SO$_4^{2-}$, HCO$_3^-$, Cl$^-$, and NH$_3$ [73]. The fate of Ni$^{2+}$, Co$^{2+}$ or NH$_4^+$ or PO$_4^{3-}$ in water should be affected both by pH and the presence of dissolved organic matter. Additionally, the adsorptive properties of biochar are affected by the presence of dissolved organic matter. DOM molecules are composed of hydrophobic segments with carboxylic acid and phenolic functionalities. These groups can affect the adsorption of metals or anions. Presence of mainly –COOH groups can be responsible rather for other than π-π interactions. DOM may compete with ions for adsorption sites but additionally, due to its chemical nature may form additional sites participating in adsorption onto TBC.

Generally, the addition of TA reduced the amount of Ni$^{2+}$ and Co$^{2+}$ adsorbed. The most sensitive to TA presence were MW during both Ni$^{2+}$ and Co$^{2+}$ adsorption and TF in Ni$^{2+}$ adsorption (Fig. 9A). The effect of TA addition onto NH$_4^+$ + PO$_4^{3-}$ adsorption was also noted but the data were different from Ni$^{2+}$ and Co$^{2+}$ adsorption. Generally, the greatest sensitivity to TA presence revealed PO$_4^{3-}$ adsorption onto MW (Fig. 9B) and lowering of adsorption capacity with increased TA concentration was noted. The positive correlation of C$_S$ of PO$_4^{3-}$ adsorption onto SS (p < 0.01) and TF (p < 0.05) was noted indicating the competition of TA and PO$_4^{3-}$ for adsorption sites onto SS and TF. The effect of DOM on NH$_4^+$ adsorption onto SS and TF was however different. The highest C$_S$ was noted when TA concentration was 50 mg L$^{-1}$ (Fig. 9B, Table S4). The data may imply that the competition between PO$_4^{3-}$ and TA for adsorption sites on mentioned TBC was observed and TA molecules were participating in further bonding of NH$_4^+$.

The greatest applicability of Temkin model was noted for the adsorption of Ni$^{2+}$ and Co$^{2+}$ onto TBC. Monolayer mechanism was noted only when Ni$^{2+}$ was adsorbed onto MW and the presence of TA changed the adsorption mechanism from DR to L, similarly to changed Ni$^{2+}$ adsorption mechanism onto SS TBC (from F to T). The data clearly indicate that the presence of natural organic matter in water altered Co$^{2+}$ and Ni$^{2+}$ adsorption changing not only the amount being adsorbed but also the mechanism. This effect, however, was both positive and negative.

**Soil application**

In the literature a great attention has been paid to the application of biochar for soils [72,73]. The potential of biochar for the transformation of heavy metals [35] or organic contaminants in the contaminated soil from unstable fractions to stable fractions is established. As a result the decreased mobility and bioavailability is observed [8]. On the other hand, biochar can be also used as fertilizer for controlled release of nutrients [18]. The studies of the behavior of TBC when used in soil with concentrated NH$_4^+$ and PO$_4^{3-}$ solutions is presented in Fig. 10 demonstrating some interesting observations. For NH$_4^+$ adsorption onto tested TBC the increase of C$_S$ with initial concentration of NH$_4^+$ was noted. However, when the initial concentration was 1000 mg L$^{-1}$, the amount of adsorbed NH$_4^+$ was lower indicating that the adsorption sites onto SS or TF were limited. Generally, the behavior of MW after addition of 750 mg L$^{-1}$ both nutrients was similar and noted Cs was significantly different from other concentrations. The lowest surface area offered significantly lower amount of adsorption sites. Generally, the amount of adsorbed PO$_4^{3-}$ was lower than NH$_4^+$ except the highest concentration.

The obtained data clearly indicate that presented TBC has a great potential to be used as a slow-release fertilizer to improve the composition of soil elements and soil fertility [64]. Additionally, the widely observed immobilization of metals onto biochar surface may be used for metal cations fixation in contaminated soil via adsorption and complexation lowering their mobility and thus bioavailability.

**Conclusions**

In this study, a novel, solvent free and sustainable approach was used for development of magnetic biochar from tea waste. Co-
adsorption of NH₄⁺ and PO₄³⁻ onto tested TBC was not favorable in comparison to Ni²⁺ and/or Co²⁺. The highest amount of NH₄⁺ was adsorbed onto SS and the highest amount of PO₄³⁻ was noted for MW. Highest removal capacity was observed for Co followed by Ni for all samples. The lowest removal capacity reported for PO₄³⁻ in case of SS and TF samples and then NH₄⁺ for MW sample. Chemisorption was the rate limiting step during adsorption Ni and Co from single solute system and mixture solution. The process of NH₄⁺ adsorption onto MW and PO₄³⁻ adsorption onto SS revealed the best fitting to Elovich model. The experimental data on Ni²⁺, Co²⁺ and Ni²⁺+Co²⁺, PO₄³⁻ and NH₄⁺ adsorption revealed good fitting to all tested adsorption models depending on TBC used indicating the complexity of the process and non-uniform properties of obtained TBC. The increase of the solution ionic strength affected both the amount of adsorbed Ni²⁺+Co²⁺ and the reaction ties of obtained TBC. The increase of the solution ionic strength altered Ni²⁺+Co²⁺ and NH₄⁺ adsorption. It is believed that the excellent results of utilization of tea waste biochar for wastewater treatment and sorption of nutrients from soil matrices can be a pathway for other food waste by considering sustainability and environmental circular economy approaches.

Data availability
The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Compliance with Ethics Requirements
This article does not contain any studies with human or animal subjects.

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 material
Supplementary data to this article can be found online at https://doi.org/10.1016/j.jare.2021.08.001.

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