scientific reports

OPEN

Engineered Mg-modified biochar-based sorbent for arsenic separation and pre-concentration

Vladimír Frišták[1]✉, Kristína Beliančínová[1], Lucia Polťáková[1], Eduardo Moreno-Jimenéz[2], Andrew R. Zimmerman[3], Libor Ďuriška[4], Ivona Černičková[4], Haywood Dail Laughinghouse IV[5] & Martin Pipíška[1]

The utilization of biochar as a relatively efficient sorbent or stationary phase for the separation and preconcentration of a wide range of analytes represents an innovative approach in current sample pretreatment methods. Appropriate pre- and post-pyrolysis modification of the input precursor and pyrolysis product, respectively, allows targeted design of the physicochemical properties and sorption characteristics of the resulting sorbent. The present work deals with the preparation of pyrolysis materials based on unmodified cattail leaf biomass (BC) and its Mg-modified analogue (MgBC) by a slow pyrolysis process at 500 °C and a residence time of 1 h in a pyrolysis reactor. Physicochemical characterization of BC and MgBC carried out by pH, total C, N, surface size analysis (SSA), ^{13}C NMR, SEM-EDX and XRD confirmed significant morphological and mineralogical differences between the prepared sorbents. By performing sorption experiments using a model anionic analyte (As) and application of Langmuir isotherm, we found that the predicted maximum sorption capacity of MgBC for As is 13.5-fold higher than that of BC. The sorption process of As by both sorbents is best described by the Sips adsorption isotherm ($R^2 \geq 0.995$) and a pseudo-nth order kinetic model ($R^2 \geq 0.997$). The optimum pH for As sorption by BC and MgBC sorbents is in the interval 5–6. The presence of competitive phosphate anions (equimolar concentration of 1:1) in the solution significantly reduces the sorption capacity of MgBC for As by 40% for BC by 70%. The presence of Cl- ions showed no significant effect on the sorption capacity of Bc and MgBC for As. Both sorbents were best recovered using 0.1 mol/L NaOH solution when the desorption efficiency for both sorbents was more than 95%. The MgBC sorbent showed 35% retention of As from the real sample in the model SPE column at a flow rate of 0.12 mL/s. Based on the obtained knowledge, it is evident that biochar-based sorbent prepared from Mg-modified precursor represents an effective sorbent for anionic forms of analytes and opens the possibility of its use also in preconcentration and separation techniques.

Keywords Biochar, As, Sorption, Pre-concentration, Green chemistry

Determination of trace concentrations of analytes is an essential requirement for several areas of human activities, therefore one of the main goals of green analytical chemistry is to develop simple, environmentally friendly, safe, selective and sensitive procedures and methodologies for the determination of selected analytes even at very low concentrations. The use of biochar as an efficient stationary phase for the separation and preconcentration of different analytes represents an innovative approach for sample pretreatment[1].

Solid phase extraction (SPE) is used to extract analytes from different types of matrices. This extraction method is often used mainly due to its speed, simplicity, relatively high efficiency and easy automation of the process. SPE as a separation method is also relatively inexpensive and allows the determination of trace concentrations in a small sample volume. Since the above-mentioned advantages, SPE very often replaces conventional liquid-liquid extraction. SPE is based on the separation of an analyte from a liquid sample. The liquid sample represents the mobile phase of the system, which passes through a solid adsorbent representing

[1]Department of Chemistry, Faculty of Education, Trnava University in Trnava, Priemyselná 4, P.O.BOX 9, Trnava SK- 91843, Slovakia. [2]Department of Agricultural and Food Chemistry, Faculty of Sciences, Universidad Autónoma de Madrid, Madrid 28049, Spain. [3]Department of Geological Sciences, University of Florida, 241 Williamson Hall, P.O.BOX 112120, Gainesville, FL 32611, USA. [4]Institute of Materials Science, Faculty of Materials Science and Technology in Trnava, Slovak University of Technology in Bratislava, J. Bottu 25, Trnava SK-917 24, Slovakia. [5]Agronomy Department, Fort Lauderdale Research and Education Center, University of Florida-IFAS, Davie, FL 33314, USA. ✉email: fristak.vladimir.jr@gmail.com

the stationary phase of the system, and the components from the liquid phase are adsorbed onto the surface of the adsorbent. Subsequently, the bound analytes are eluted from the sorbent into a suitable solvent. The analytes must have a higher affinity for the sorbent than for the liquid phase from which they are adsorbed[2].

Sorbents or stationary phases used in SPE are gaining increasing attention because they play a key role in achieving higher purification and sample treatment efficiencies for trace analysis of a wide range of analytes in complex matrices[2]. Sorbents are broadly classified into three main material groups namely oxides, sorbents with low specificity for a given analyte (general purpose) and sorbents highly specific for a given analyte structure[3]. In recent years, many other sorbents have been investigated and put into practice to replace traditional sorbents in the extraction of target analytes[4]. These are mainly modern and low-cost sorbents based on waste materials, carbonaceous materials as well as biosorbents.

Biochar represents a porous carbonaceous material with high degree of aromatic structure, which is produced by the thermal decomposition (pyrolysis) of plant biomass or animal origin in the absence of oxygen or in an oxygen-limited environment. Biochar contains predominantly C, H and O and in lower concentrations N, S, P, K, Na, Mg, Al, Fe, Ca and Si[5]. Pyrolysis is an anaerobic thermochemical process that results in the decomposition of organic matter into gas, bio-oil and a solid by-product- biochar[6]. Despite the absence of oxygen, partial oxidation can occur during pyrolysis, e.g. due to the natural oxygen content of the biomass[7]. An important property of biochar that affects its application as a sorbent in analyte separation processes is its surface charge. As we know well the pH of the solution or sample significantly affects the surface charge of biochar. The properties of biochar can be modified by pre-pyrolysis as well as post-pyrolysis treatment procedures (so-called modification). Pre-pyrolysis treatment is the treatment of the input precursor (biomass) by a process of biological, chemical or physical activation. Temperature and pressure do not usually form the cranking parameters. The biomass thus modified is subsequently subjected to pyrolysis treatment. In the case of post-pyrolysis treatment, the natural precursor (raw biomass) enters the thermochemical conversion process without any activation. After pyrolysis treatment, the resulting product (biochar) is subjected to biological, chemical or physical modification. Modification of biomass by appropriate physical as well as chemical processes has proven to be a suitable tool for achieving the observed material characteristics of the resulting biochar[8]. During the modification of biochar by acids, ash residues and impurities are removed from the surface and new carboxyl groups are bound or created, which give the final product a higher affinity for the cations of the analytes[9]. Modifications using an oxidizing agent can be carried out using hydrogen peroxide (H_2O_2) or nitric acid (HNO_3) at low temperatures. The use of HNO_3 reduces the specific surface area and pore volume due to the destruction of the porous structure of biochar. Sulfurization by SO_2 or H_2S can also have a destructive effect on the porosity, but can, for example, significantly increase the sorption capacity for Hg. Nitrogenating or nitrogen modification is mainly carried out by treating biochar with ammonia (NH_3) in the gaseous state and is used to achieve polarity and alkalinity enhancement to increase the sorption capacity but also the catalytic properties of pyrolysis materials[7]. An important role in the modification of biochar or its precursor is the formation of suitable mineral composites that can serve as active sorption sites for oxyanions, whose sorption separation in the case of unmodified materials is negligible.

Since most scientific studies are devoted to the characterization of biochar as a sorbent under embedded (static) conditions and only a limiting literature is available on SPE applications, this line of scientific research is highly relevant and in demand. In the work of Zhang et al[10]., the authors prepared magnetic biochar obtained by pyrolysis of bamboo and wood-based feedstock precursors, followed by a magnetization process. The prepared materials were used as efficient sorbents for SPE-extraction of fentanyl analogues from urine. Ozdes et al[11]. describe the preparation of biochar from melon peels that were modified with $CoFe_2O_4$ (MPBC/ $CoFe_2O_4$). The prepared material was characterized as an SPE-sorbent for the separation and preconcentration of selected heavy metal ions such as Cu^{2+}, Cd^{2+} and Pb^{2+}. Rovani et al[12]. highlighted the thermochemical treatment of coffee waste and eucalyptus sawdust to produce sorbents for the preconcentration of 17β-oestradiol from aqueous solutions. Similarly, Duran et al[13]. in their work used magnetic biochar prepared from *Alnus glutinosa* (sticky alder), which was subsequently modified with Fe_3O_4/SiO_2-cetyltrimethylammonium bromide to a magnetic analogue for an SPE cartridge useful for the separation of Cu^{2+}, Cd^{2+} and Pb^{2+} ions from water samples and fruit juices.

Based on the above, the main objective of the work was to verify the effectiveness of Mg- pre-pyrolysis modification of the feed precursor to increase the sorption efficiency of the prepared biochar for AsO_4^{3-} oxyanions. The choice of arsenic as a model analyte represents the most insight into the chemical speciation, the form as well as the toxicological profile of this semi-metal. From the point of view of its occurrence and preconcentration in surface waters, it represents an interesting analyte, the detection of which is fully desirable in all areas of health and safety assurance. Another important objective was to evaluate the effectiveness of using this material as a packing for pilot SPE preconcentration columns.

Materials and methods

Preparation of biochar-based sorbents

For biochar production, leaf biomass of cattail (*Typha latifolia*) collected in the South Florida Watershed was used as the input precursor. The plant biomass was subsequently washed in deionized water, chopped to approximately equal size, and dried for 7 days. The biomass was then divided into two fractions, with the first fraction subjected to chemical pre-pyrolysis modification with a 1.5 mol/L $MgCl_2$ solution at a 1:10 ratio (biomass: modifying agent). The prepared unmodified as well as the Mg-pre-pyrolysis modified feedstock precursor were subjected to a slow pyrolysis process under analogous conditions, namely pyrolysis temperature of 500 °C, biomass residence time in the reactor of 60 min and provision of an anoxic atmosphere with gaseous N_2 in the inlet pyrolysis reactor. The prepared pyrolysis products based on unmodified biomass (BC) and Mg-modified cattail leaf biomass (MgBC) were ground and using standard sieves, a fraction of 0.25–1 mm was obtained, which was subsequently stripped of residual moisture by drying at 50 °C for 24 h.

Physico-chemical characterisation

The basic physicochemical parameters of BC and MgBC were obtained by determining the active pH in deionized water (v/v 1/10, shaking for 1 h at 45 rpm and stabilization for 1 h) using a pH/EC multimeter 3420 (WTW, Germany), total organic C and N content using a CN analyser LECO CN-628 (St. Joseph, MI, USA). Water-extractable forms of AsO_4^{3-}, PO_4^{3-} and NO_3^- were determined in aqueous extracts of BC and MgBC (v/v 1/40) after 24 h extraction time at 22 °C, 150 rpm using AA3 HR autoanalyzer (SEAL Analytical, Wisconsin, USA) and Ecaflow (ISTRAN, Slovakia). The determination of the point of zero charge (pH_{PZC}) was carried out using a series of 0.01 mol/l NaCl solutions with pH ranging from 1 to 12. pH values were adjusted using 0.1 mol/l HCl and 0.1 mol/l NaOH and pH_{PZC} was determined using a pH/EC multimeter (HANNA, USA). The specific surface area (SSA) of BC and MgBC samples was determined by CO_2 adsorption method using Quantrachrome AsiQwin TM (Boyton Beach, Florida, USA). Characterization of the morphology and structure of BC and MgBC samples was performed using a JEOL JSM-7600 F scanning electron microscope (SEM) (Tokyo, Japan). The microscope was operated at an accelerating voltage of 20 kV in the secondary electron mode (LEI). Energy dispersive X-ray spectroscopy (EDX) was used for elemental mapping using an Oxford Instruments X-max 50 spectrometer. The ^{13}C (100.73 MHz) CPMAS NMR spectra of BC and MgBC samples were obtained with a Bruker AV WB 400 spectrometer at 300 K using a 4 mm three-channel probe head. X-ray diffraction (XRD) analysis was performed using a Philips PW 1830 diffractometer (Philips N.V., Amsterdam, The Netherlands) with iron-filtered Co Kα1,2 radiation to determine the crystal structure of the BC and MgBC samples. Diffractograms were obtained over a range of diffraction angles (2θ) between 10 and 80° with a step size of 0.02° and an exposure time of 10 s per step.

Batch sorption experiments

Effect of sorbate's initial concentration

To describe the sorption properties of the investigated BC and MgBC adsorbents, we used AsO_4^{3-} as a model sorbate present in aqueous solution predominantly in the anionic form. To investigate the dependence of the sorption capacity of the studied BC and MgBC sorbents on the initial As concentration in solution, we worked with solutions with As concentrations of 1, 5, 10, 20 and 50 mg/L, with pH values 5–6. We weighed 0.1 g of BC or MgBC sorbent into the centrifuge tubes and then added 7.5 mL of As solution. The obtained suspensions were stirred for 24 h on a laboratory shaker (Multi RS-60, Biosan, Lithuania). After a contact time of 24 h, we separated the supernatant from the sediment by centrifugation for 10 min and at 4000 rpm (EBA 200 S, Hettich, Germany). After removal from the centrifuge, we filtered the supernatant through a 0.45 µm nylon syringe filter. After filtering, we detected pH values in the supernatants using a multimeter (Multi 3420, WTW, Germany). These samples were then analyzed using flow stripping chronopotentiometry (EcaFlow 150 with E-T/Au type electrode, Istran, Slovakia) with application of a gold Et-Au working electrode The electrochemical determination itself followed the manufacturer's prescribed methodology for the determination of total As in all types of aqueous samples-drinking water, groundwater, surface water as well as wastewater (Application Note No. 40). The principle of the determination is based on the use of stripping chronopotentiometry (SCP) where As(III) as well as As(V) is electrochemically separated on the working electrode as elemental arsenic according to the following redox reactions:

$$AsO_3^{3-} + 6H^+ \rightarrow As^0 + 3H_2O - 3e^- \tag{1}$$

$$AsO_4^{3-} + 8H^+ \rightarrow As^0 + 4H_2O - 5e^- \tag{2}$$

In the next step, the deposit of the excluded As is dissolved by a constant current, registering the obtained analytical signal. The chronopotentiogram is used to calculate the concentration of arsenic in the supernatant sample after sorption as the equilibrium concentration of As. To calculate the amount of As sorbed by BC- and MgBC-based sorbents, we assumed the following basic relationship:

$$Q_{eq} = (C_0 - C_{eq}) * V/m \tag{3}$$

where Q_{eq} expresses the amount of As adsorbed (mg/g), C_0 expresses the initial concentration of As in solution (mg/L), C_{eq} represents the equilibrium concentration of As (mg/L), V is the volume of the solution (L) and $m$is the mass of the adsorbent (g)[14].

For sorption data characterization, the empirical equations of the models of Langmuir[15], Freundlich[16], and Sips (combined Langmuir–Freundlich model)[17] adsorption isotherms were applied. The adsorption isotherm parameters were obtained using non-linear regression via the software: MicroCal Origin 8.0 Professional (OriginLab Corporation, Northampton, MA, USA).

The model of Langmuir isotherm (Eq. (4)) is given by the following empirical equation:

$$Q_{eq} = \frac{(bQ_{max}C_{eq})}{((1 + bC_{eq})} \tag{4}$$

where b represents the coefficient characterizing the affinity of material to As ions in the matrix (L/mg), Q_{eq} is the amount of adsorbed As at time of equilibrium (mg/g), C_{eq} is As concentration in equilibrium (mg/L) and Q_{max} is the maximum sorption capacity at saturated sorbent binding sites (mg/g).

The Freundlich adsorption model (Eq. (5)) is given by the following equation:

$$Q_{eq} = KC_{eq}^{1/n} \tag{5}$$

where n and K represent the Freundlich empirical constants characterizing intensity of sorption (L/g), C_{eq} is a As concentration in equilibrium (mg/L) and Q_{eq} is the amount of sorbed As ions at equilibrium (mg/g).

The combined form of Langmuir and Freundlich expressions (Eq. (6)) (Sips isotherm) is given by the equation:

$$Q_{eq} = \frac{(Q_m(bC_{eq})^{1/n})}{((1 + (bC_{eq})^{1/n})} \tag{6}$$

where Q_{eq} is the amount of sorbed As at equilibrium (mg/g), b is the Sips constant characterizing sorbent affinity to As ions in solution (L/mg), C_{eq} represents the As equilibrium concentration in solution (mg/L), n is the index of heterogeneity and Q_m is the monolayer sorption capacity at saturated sorbent binding sites (mg/g).

Effect of contact time

To observe the dependence of the sorption capacity of BC and MgBC for As on contact time, we used an As solution with a concentration of 10 mg/L and a pH value 5–6. We weighed 0.1 g of BC and MgBC sorbent, respectively, into centrifuge tubes and added 7.5 mL of As solution. The As concentration in the solution was measured at time intervals of 5, 10, 30, 60, 120, 240, 360, 1440 and 2880 min using a flow stripping chronopotentiometry (EcaFlow 150 with E-T/Au type electrode, ISTRAN, Slovakia) considering the sample treatment time (centrifugation). The measurement was carried out in three repetitions. The obtained experimental kinetic data on the sorption capacity of BC and MgBC were subsequently described by pseudo-first, pseudo-second and pseudo-n-th order kinetic models[8]. The kinetic parameters were obtained by the software: MicroCal Origin 8.0 Professional (OriginLab Corporation, Northampton, MA, USA).

The pseudo-first order model (Eq. (7)) (Lagergren equation) can be defined as:

$$\frac{dQ_t}{dt} = k_1(Q_{eq} - Q_t) \tag{7}$$

where Q_{eq} represents the value of As sorbed at equilibrium time (mg/g), Q_t is the amount of As sorbed at time t (mg/g), and k_1 is the constant rate of pseudo-first order action (1/min).

The pseudo-second order equation (Eq. (8)) can be defined as:

$$\frac{dQ_t}{dt} = k_2(Q_{eq} - Q_t)^2 \tag{8}$$

where Q_t and Q_{eq} have equal meanings as in the pseudo-first order model and k_2 is the constant rate of the pseudo-second order (g/mg/min).

The pseudo-n^{th}order[18] (Eq. (9)) can be defined as:

$$\frac{dQ_t}{dt} = k_3\frac{(Q_{eq}^n - Q_t^n)}{Q^{n-1}} \tag{9}$$

where n is the order of rate equation, Q_{eq} and Q_t have the same meanings as in the pseudo-first order, and k_3 represents the constant rate of the pseudo-n^{th} order (g/mg min^{-1}).

Effect of pH

To investigate the effect of pH on As sorption by BC and MgBC sorbents, we used As solutions with a concentration of 10 mg/L, pH values of 3, 4, 5, 6, 7 and 8 adjusted with 1 mol/L HCl and 1 mol/L NaOH. We weighed 0.1 g of sorbent BC and MgBC, respectively, into centrifuge tubes and added 7.5 mL of As solution. The obtained suspensions were stirred on a shaker (Multi RS-60, Biosan, Lithuania) for 24 h, 23 °C and then centrifuged at 4000 rpm for 10 min. After sediment separation, we filtered the obtained supernatant through a 0.45 µm nylon syringe filter and measured the pHeq value using a Multi 3420 multimeter (WTW, Germany). The concentration of As in the samples was quantified electrochemically in a similar manner as in the previous section. The experiment was carried out in 3 replicates. To determine the chemical speciation of arsenic, i.e. to determine the ratio of all ionic forms of arsenic in aqueous solutions, the Visual MINTEQ program (version 3.01) was used, based on the values of the stability constants of the log K complexes and on the thermodynamic characteristics of dHr under defined environmental conditions (pH, ionic strength, concentration, temperature).

Effect of competitive co-ions

We used Cl^- (NaCl) and PO_4^{3-} ($(NH_4)_2HPO_4$) ions at concentrations of 5 mg/L, 10 mg/L and 20 mg/L in As solutions (10 mg/L) to investigate the effect of ion competence of ions frequently present in waters and aqueous samples, respectively. The pH of the solutions was adjusted with 1 mol/L HCL and 1 mol/L NaOH to values in the range of 5–6. We weighed 0.1 g of BC and MgBC sorbent, respectively, into the tubes and added 7.5 mL of the solution. The obtained suspensions were stirred for 24 h on a laboratory shaker (Multi RS-6, Biosan, Lithuania) and then the supernatant was separated from the sediment by centrifugation, which was filtered through a 0.45 µm nylon syringe filter. Samples were analyzed as in the previous sections using an electrochemical analyser (EcaFlow 150 with E-T/Au type electrode, ISTRAN, Slovakia).

Regeneration of sorbents
To confirm the possibility of BC and MgBC regeneration after As sorption, we used deionized water, 1 mol/L HCl and 1 mol/L NaOH as desorption reagents. The BC and MgBC sorbents after previous As sorption (c_0 10 mg/L) were dried to constant weight at 60 °C for 24 h. To the weighed sorbent, 7.5 mL of desorption reagent was added, and the obtained suspension was stirred for 24 h at 45 rpm on a laboratory shaker (Multi RS-60, Biosan, Lithuania). The obtained supernatant was filtered through a 0.45 µm nylon syringe filter and subjected to electrochemical analysis for the determination of unsorbed As (EcaFlow 150 with E-T/Au type electrode, ISTRAN, Slovakia).

Applicability of sorbents as SPE column cartridge
To confirm the applicability of MgBC as a SPE column cartridge, we used a model column with a total volume of 25 mL filled with 1 g of sorbent anchored with glass wool. To verify the suitability of the sorbent as SPE column packing, liquid laboratory waste from previous experiments was used as a real sample. The exact concentration of As in the solution as well as in the eluate coming out of the column was determined by As determination with an electrochemical analyser as in the previous case. The flow rate of the dosed solution in column was 0.12 mL/s.

Results and discussion
Sorbents characterization
The active pH for the MgBC-based sorbent indicated a higher value (9.85) compared to BC (8.21) (Table 1). The authors in the work of Jindo et al[19]. determined similar active pH values for unmodified biochar based on rice straw and oak wood chips, respectively. The higher alkaline character of MgBC resulted from the pre-pyrolysis treatment of the initial precursor of cattail leaves in $MgCl_2$ solution and the subsequent thermochemical conversion carried out at 500 °C. It was also found that the pH_{PZC} of the BC increased from 7.5 to 8.4 for the MgBC. The point of zero charge (pH_{PZC}) of biochar represents the pH of the solution, at which the surface charge of biochar is zero. If we have a solution with a pH ˃ pH_{PZC}, the biochar will be negatively charged and will then bind to its surface cations of analytes such as Cu^{2+}, Pd^{2+} or Hg^{2+}. If, on the other hand, we have a solution with pH ˂ pHPZC, the surface charge of biochar will be positive and will bind anionic forms such as $HAsO_4^{2-}$ or $HCrO_4^{2-}$. At higher pyrolysis temperature, the amount of negatively charged functional groups (-COO^-, -COH,-OH) decreases as well, leading to an increase in pHPZC[20]. Elemental analysis of BC and MgBC confirmed a higher content of total C in the unmodified biochar (69.97%) than in the Mg-modified biochar (58.93%). The total amount of N was 1.61% and 2.27% in the BC and MgBC samples, respectively. In the work of Saleh et al[21]. for Mg-modification of biomass feedstock, the authors confirmed a similar trend in the decrease of total N in the modified pyrolysis product compared to unmodified biochar. Determination of surface area by CO_2 adsorption by BC and MgBC materials followed by application of mathematical models of BET adsorption model indicated a decrease in SSA value from 282.4 m^2/g for BC to 256.9 m^2/g for MgBC because of Mg impregnation of biomass. The decrease in SSA was also evident in the determination of micropore volume. As is evident from the determined parameters Mg-modification of cattail biomass with subsequent pyrolysis led to the closure of some plant braid structures and thus blocking the forming porosity. The total micropore volume was 0.100 mL/g at BC and 0.092 mL/g at MgBC. Determination of the readily soluble forms of P and N as the respective cationic and anionic chemical forms confirmed negligible concentrations. Determination of the total As concentration confirmed for both BC and MgBC materials concentrations lower than the quantification limit (0.05 µg/g) for the analytical method used.

The ^{13}C nuclear magnetic resonance spectroscopy results (Fig. 1A, B) for both BC and MgBC solid carbon samples are of the same nature. The spectra are dominated by an intense peak in the chemical shift region around $\delta = 130$ ppm, indicating the presence of carbon bound in the aromatic structures. On detailed description of the NMR spectra obtained, it is evident that the majoritarian peak of MgBC has a straight-line shape in contrast to BC and the upper part of the left arm. The results of Singh et al[22]. demonstrated that this phenomenon can occur if lignin and tannin are retained in the sample, an oxygen-substituted aryl structure is formed, or oxygen substitution of aromatic C has occurred. We also observe two minor peaks in the spectra. The first in the $\delta = 30$ ppm region, characteristic of the presence of alkyl structures, and the second in the $\delta = 200$–230 ppm

	BC	MgBC
pH	8.21 + 0.50	9.85 + 0.50
C (%)	69.97	59.93
N (%)	1.61	2.27
Specific surface area (m^2/g)	282.4	256.9
V_{pores} (mL/g)	0.100	0.092
pH_{PZC}	7.50	8.40
AsO_4^{3-} (µg/g)	< 0.05	< 0.05
PO_4^{3-} (µg/g)	50.0 ± 0.5	3.8 ± 0.7
NO_3^- (µg/g)	1.3 ± 0.2	2.8 ± 0.2
NH_4^+ (µg/g)	6.2 ± 0.2	9.0 ± 0.8

Table 1. Basic physicochemical characteristics of BC and MgBC. * measurement of the representative sample in one repetition.

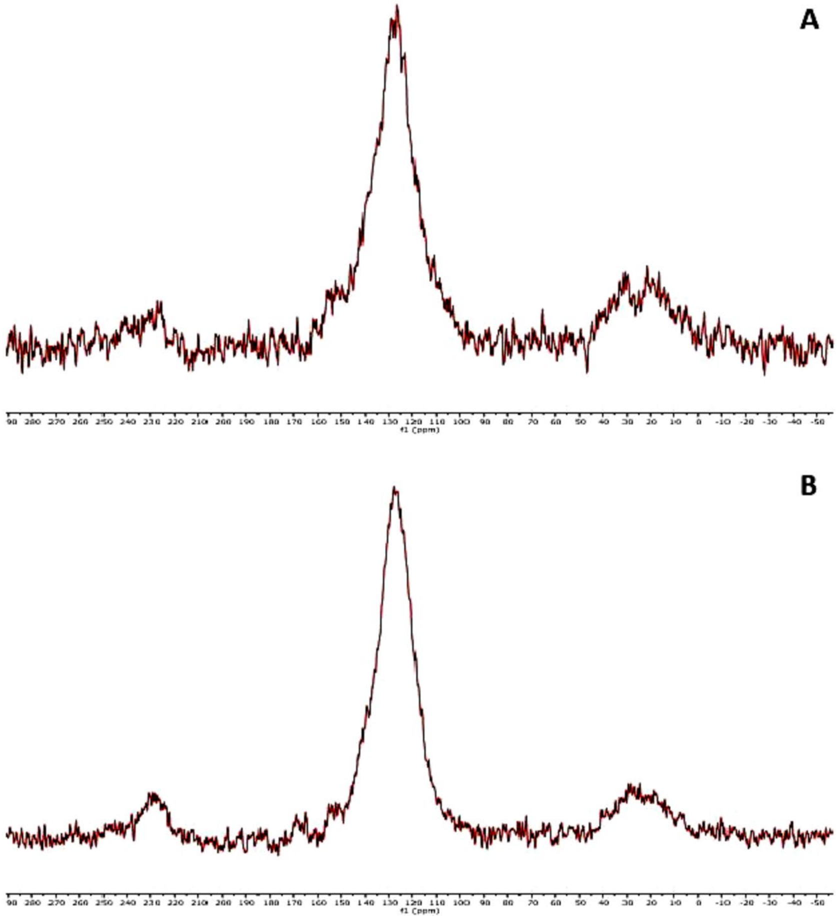

Fig. 1. ^{13}C-NMR spectra of BC (**A**) and MgBC (**B**).

region, characteristic of the presence of carbonyl and carboxyl structures. The carbon present in alkyl structures represents the degradable part of biochar, which acts as a substrate in the soil and at the same time is a source of C and energy for microorganisms[19]. Scanning electron microscopy of BC and MgBC at 250× (Fig. 2A, C) and 1000× (Fig. 2B, D) magnification confirmed the porous nature of both samples. In the case of MgBC, the presence of needle-like crystalline structures is characteristic, which we predict the formation of Mg mineral composites on the surfaces of modified biochar.

For this purpose, we also chose to include energy-dispersive X-ray analysis (EDX), which confirms to us not only the efficiency of pyrolysis (Fig. 3A, B) but also the Mg-modification itself (Fig. 3C, D,E, F) with the formation of key chemical forms of magnesium on the surface of the MgBC sorbent. Elemental mapping revealed the formation of Mg composites with Cl, O, H, C. Similar forms were observed for Mg-modification of biochar based on walnut shells as input precursor produced at 500 °C[23]. A detailed picture of the mineralogical constitution of BC and especially MgBC sorbents was obtained by XRD analysis. X-ray diffraction analysis of BC and MgBC samples (Fig. 4A, B) confirmed the efficiency of Mg-chemical modification of the feed precursor and the creation of new chemical forms of Mg in the MgBC pyrolysis product (Fig. 3C). As evident from the obtained diffraction spectra, the BC sample contains a qualitatively rather conventional mineral representation in the context of biochar samples produced from plant residues[24]. The obtained characteristic peaks in the X-ray diffractogram of the BC sample in the range of 5–80° were relatively narrow, which refutes the nanocrystalline nature of the mineral components. The detection of graphene structures in the BC sample was more pronounced in terms of the peaks present at $2\theta = 18.5$, 35 and 54. The peak at $2\theta = 29.5$ is attributed to the hexagonal structure of calcite ($CaCO_3$) based on the comparison of the datasets with the database, whose intensity decreased for the MgBC sample (Fig. 4B) due to the formation of new composites $CaCO_3 + CH_7ClMg_2O_7$ i.e. calcite and chloroartinite ($Mg_2(CO_3)Cl(OH){-}3H_2O$) as the major mineral form of the Mg present in the MgBC structure. Chloroartinite as a chemical form formed at lower pyrolysis temperatures (400–500 °C) has been confirmed as well as an intermediate form of Mg in the pyrolysis of Mg-modified beech wood chips in the temperature range of 350–700 °C[8]. Similarly, the X-ray diffractogram of MgBC shows the presence of a peak at $2\theta = 43$ corresponding to the cubic phase of MgO (periclase). In both spectra there are further characteristic peaks corresponding to the cubic phases of sylvinite (KCl), halite (NaCl), zeolite (SiO_2) as well as the orthorhombic structure of boehmite (AlO(OH)).

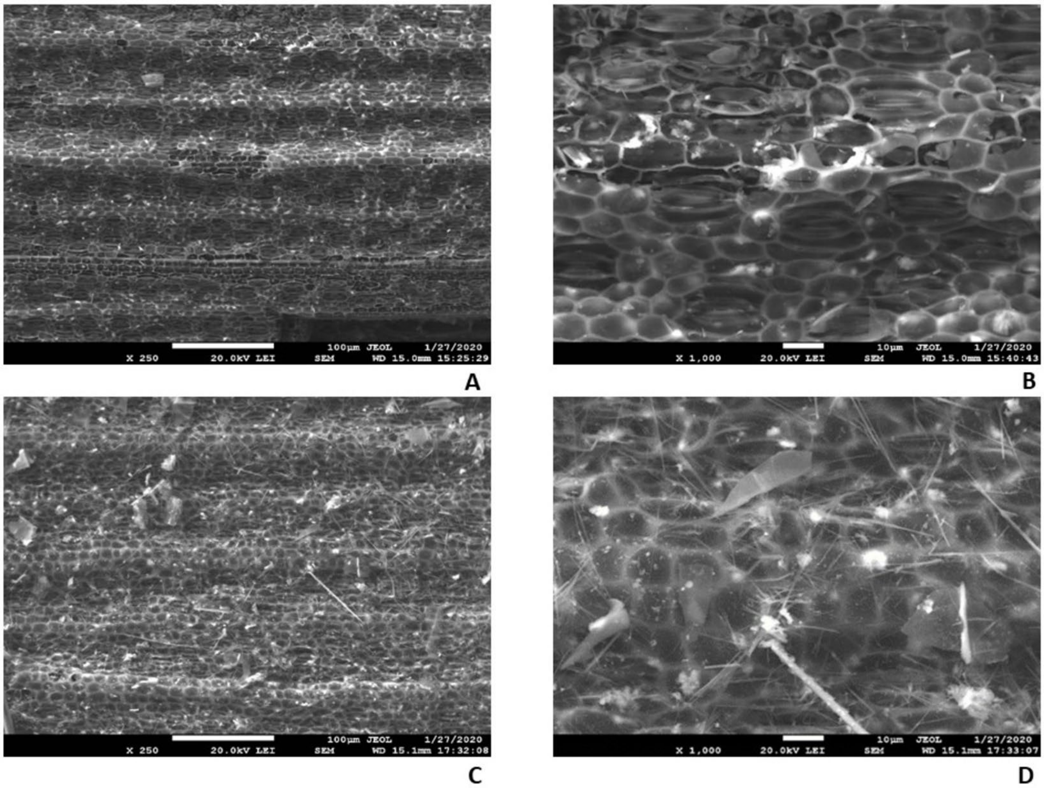

Fig. 2. SEM images of BC (**A**, **B**) and MgBC (**C**, **D**) at 250x and 1000x magnification.

Sorption testing

To determine the dependence of the sorption capacity for BC and MgBC sorbents on the initial As concentration in solution, we performed an experiment using As solutions with a concentration range of 1–50 mg/L with a pH value in the range of 5–6 and a contact time of 24 h. The values obtained confirmed only minimal sorption of As by the BC sorbent (Fig. 5A). The obtained experimental data were described using the mathematical model of Langmuir, Freundlich and Sips (Langmuir-Freundlich) adsorption isotherm (Fig. 5A, B). For both sorbents, the sorption data were best described by the Sips adsorption isotherm with an R^2 (coefficient of determination) value for BC of 0.99597 and for MgBC of 0.99521. The Sips model generally represents a three-parameter isotherm as a combination of the Langmuir and Freundlich models. The model ideally describes the sorption process of analytes onto sorbents of heterogeneous nature and heterogeneous surfaces, which the investigated BC- and MgBC-based sorbents actually are. The maximum experimental Q_{eq} As value for MgBC was in the range of 2.25–2.5 mg/g, which represents a significant difference from the maximum experimental Q_{eq} value for BC of 0.0375 mg/g. The predicted value of the maximum sorption capacity $Q_{\max}$calculated from the Langmuir model for MgBC was 13.5-fold higher compared to BC. According to Yan et al[25]., the maximum sorption capacity of biochar modified with $ZnCl_2$for As is 17.2 mg/g. Zhu et al[26]. in their work, reported that the modification of biochar by forming α-FeOOH composites leads to an increase in the value of the maximum sorption capacity for As to 78.30 mg/g. Zhu et al[26]. as well as Van Vihn et al[27]. reported that the sorption process of As onto $Zn(NO_3)_2$-modified biochar is best described by the Langmuir isotherm with R^2= 0.93. On the other hand, Xia et al[29]. reported in their work that the sorption of As by biochar modified with $ZnCl_2$ is most effectively described by the Freundlich adsorption isotherm with R_2 ˃ 0.99.

To determine the dependence of the BC and MgBC sorption capacity for As on the contact time between sorbent and sorbate, we used an As solution with a concentration of 10 mg/L and a contact time in the range of 5–2880 min. The experimental data obtained were described by pseudo-first-, pseudo-second- and pseudo-n$^{\mathrm{th}}$-order kinetic models (Table 2). The As sorption process for both sorbents is best described by the pseudo-n$^{\mathrm{th}}$ order kinetic model with an R^2 value of 0.9989 for BC and 0.9967 for MgBC. The experimental results show that the optimum contact time to reach saturation of the sorbent with sorbate is 24 h with Q_{eq} = 0.035 ± 0.003 mg/g for BC and Q_{eq}= 0.63 ± 0.02 mg/g for MgBC. For this reason, we also used this time in further experiments. Sorption of As by MgBC-based sorbent proceeds in two steps. The beginning is dominated by a relatively fast initial phase that lasts for 6 h during which the maximum number of binding sites is occupied. A second, slower and quantitatively less significant phase involves saturation of the sorbent with arsenic ions. The same sorption process from a kinetic point of view was also characterized in the work by Wang et al[28].. Other authors[29–31]reported in their works that the percentage of As removed by biochar-based sorbents prepared from banana peels, fruit stones and residues after biogas production increases with increasing sorption time. In contrast to our results, Xia et al[29]. reported that the kinetics of As sorption by $ZnCl_2$-modified biochars is best

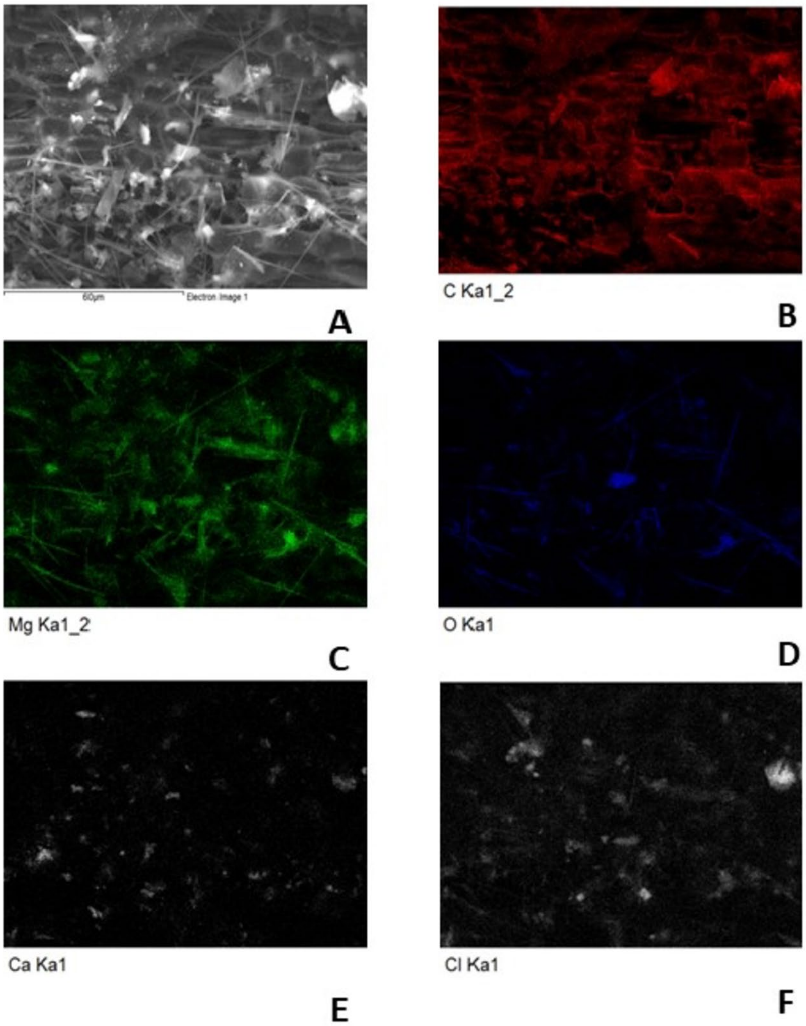

Fig. 3. EDX surface analysis of MgBC (**A**) with elemental mapping of C (**B**), Mg (**C**), O (**D**), Ca (**E**) and Cl (**F**).

described by a pseudo-second-order kinetic model. This result was also reached by Zhu et al[26].. Authors sorbed As onto biochar modified with α-FeOOH prepared by pyrolysis of wheat straw.

..

To investigate the effect of pH on the As sorption process, we used an As solution with a concentration of 10 mg/L whose pH ranged from 3 to 8 and with a contact time of 24 h. From the experimental results, we found the effect of initial pH of the system on the equilibrium amount of As sorbed by BC and MgBC sorbents (Fig. 6A, B) and the change of pH with time (Fig. 6C). By observing the effect of pH on the equilibrium amount of sorbed As, we found that the Q_{eq} value decreased with increasing initial pH value for BC sorbent and remained approximately the same for MgBC sorbent. The minimum change occurred in the pH 3–4 interval when Q_{eq}increased slightly, stabilized and then had a decreasing trend at pH 7. These results suggest that the optimum pH for As sorption is in the interval 5–6. Yan et al[25]. who used biochar modified with $ZnCl_2$concluded that the sorption capacity decreases with increasing pH. Lata et al[30]. reasoned this that the change in pH changed the surface charge of biochar to negative, which caused the surface of biochar to repel sorbate. Only Rahman et al[31]. reported that the pH of the solution had minimal effect on the sorption of As. For this experiment, the authors used biochar modified with $FeSO_4$ with a study pH range of 2–9. This can be attributed to the large surface area of the biochar and the change in chemical speciation of arsenic because of the change in reaction pH. The kinetic assessment of the pH change (Fig. 6C) confirmed that the pH increased from an initial value of 5.8 to 8 after only 30 min when As was sorbed with BC sorbent. After 60 min, the pH change slowed down and at the end of the experiment, after 48 h, it was 9.2. For MgBC, the change was more rapid, as after 5 min the pH had already risen to 9.2 and the value at the end of the experiment was 10. In silico spectroscopic analysis performed using Visual MINTEQ (version 3. 01), which is based on the values of the stability constants of the log K complexes and on the thermodynamic characteristics of dHr under defined environmental conditions (Fig. 6D), confirmed to us that, under our experimental conditions, As at pH 3 in aqueous solution occurs in the form of H_3AsO_4 (18%) and $H_2AsO_4^-$ (82%). The concentration of H_3AsO_4 decreases with increasing pH value. At pH 4, a dissociated

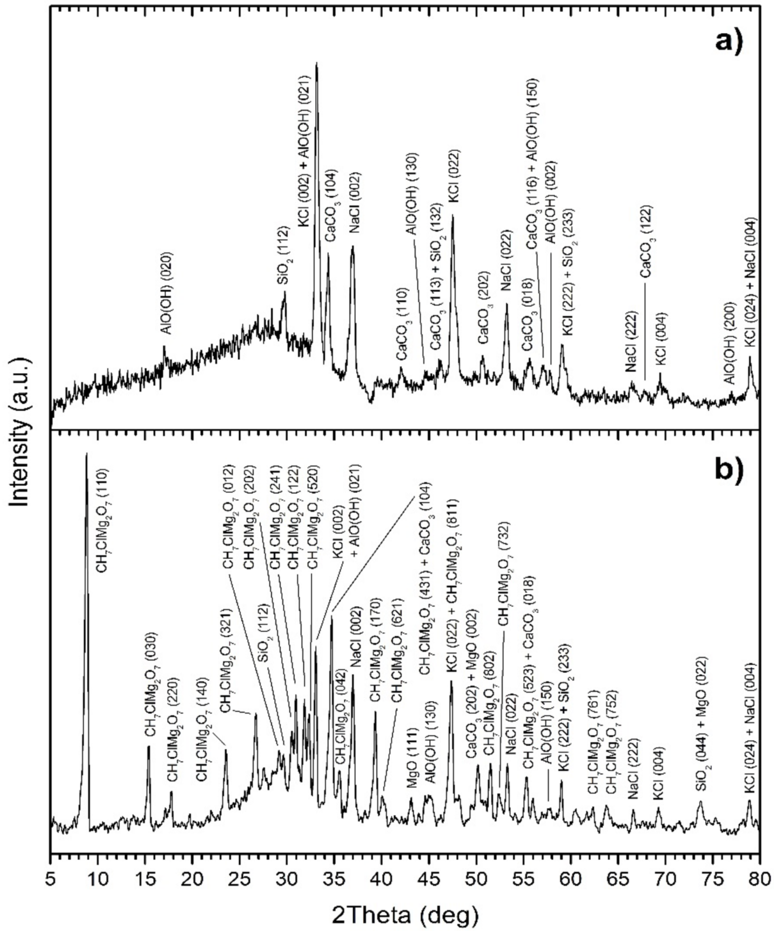

Fig. 4. XRD diffraction spectra of BC (**A**) and MgBC (**B**).

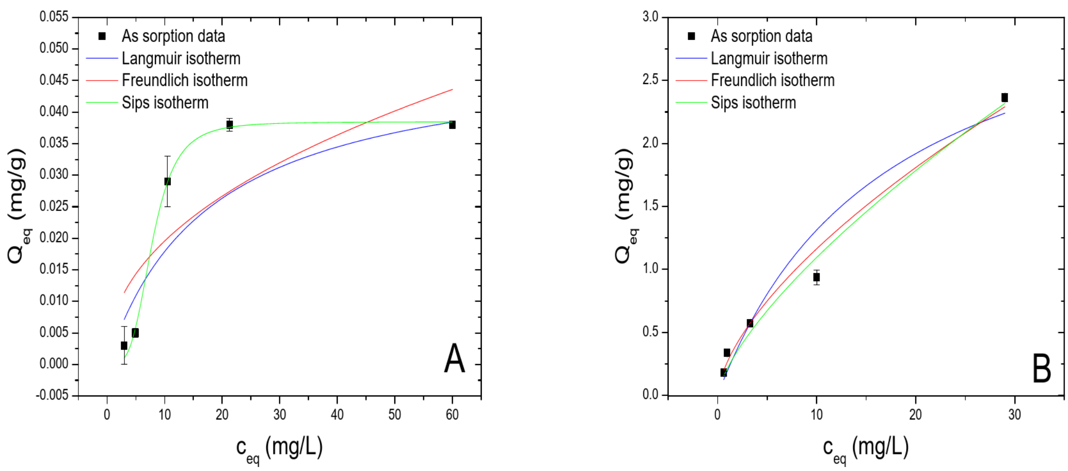

Fig. 5. Experimental data of the equilibrium sorption process of As by BC (**A**) and MgBC (**B**) based sorbents described by Langmuir, Freundlich and Sips adsorption isotherm models.

form of $HAsO_4^{2-}$ begins to appear, which becomes dominant with increasing pH. The dissociated form $H_2AsO_4^{-}$, which was dominant at pH 3, reached almost 100% at pH 4–6, but after pH 6 its content in the solution began to decrease and by pH 8 it represented less than 10% of the total As content of the solution. According to these facts, we found that the As solution at the beginning of the experiment contained As in the majority form $H_2AsO_4^{-}$. As the pH increased rapidly, after a short time the dominant dissociated form was already $HAsO_4^{2-}$.

applied model	parameter	BC	MgBC
kinetic model of pseudo-first order	Q_{eq} (mg/g)	0,100054	0,4515
	k_1 (g/mg/min)	0,0002847	0,01189
	R^2	0,98074	0,95471
kinetic model of pseudo-second order	Q_{eq} (mg/g)	0,20142	0,53581
	k_2 (g/mg/min)	0,0006954	0,02387
	R^2	0,97495	0,97027
kinetic model of pseudo-nth order	Q_{eq} (mg/g)	0,35965	0,56745
	k_3 (g/mg/min)	0,00566	0,00251
	n	0,03976	1,6229
	R^2	0,99886	0,99672

Table 2. Parameters of pseudo-first-, -second- and nth-order kinetic models for the description of as sorption by BC and MgBC (c_0 10 mg/L, sorbent/reaction solution ratio: 1/75, pH 5–6, 22 ± 2 °C′, 45 rpm).

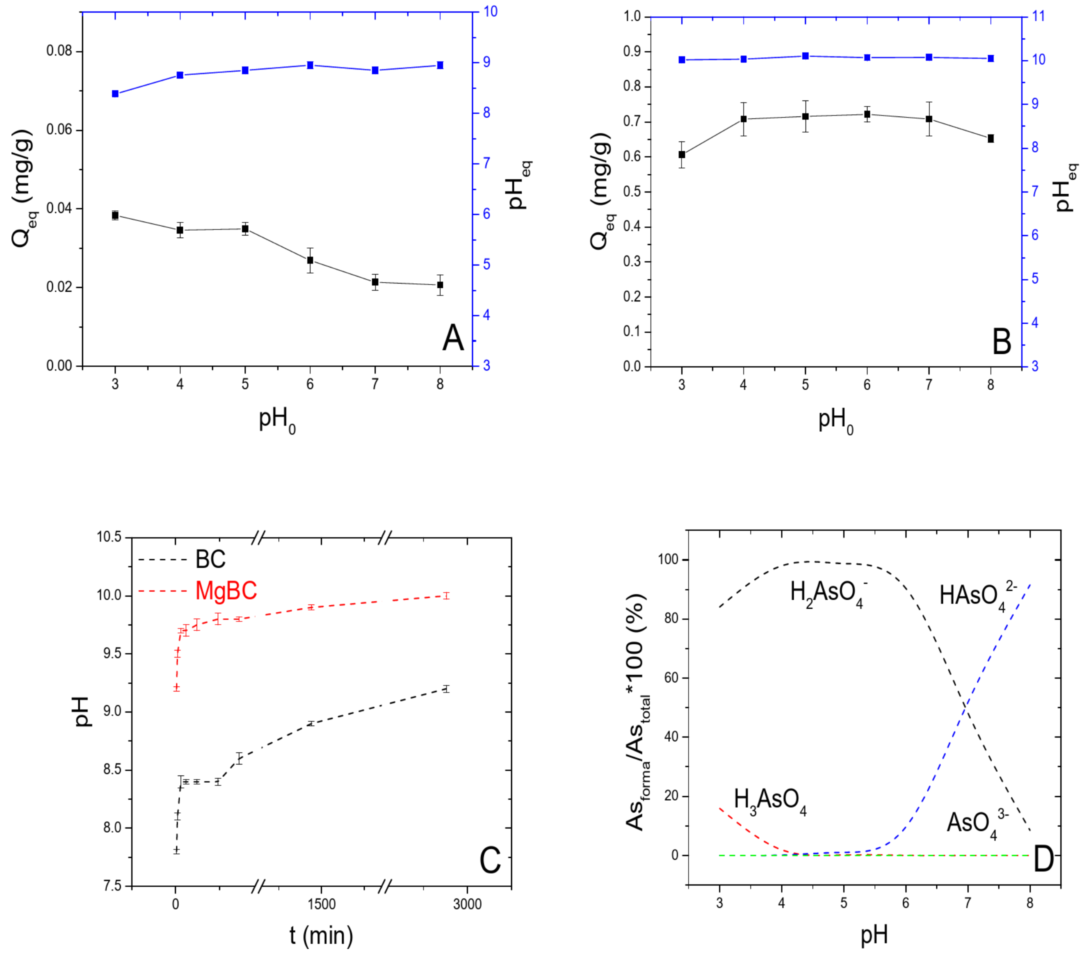

Fig. 6. Dependence of As-sorption capacity (-) of BC-based (**A**) and MgBC-based (**B**) sorbents and equilibrium pH (-) on the initial pH value. Effect of contact time between sorbent and sorbate on pH change (pH_0 5.8) (**C**), in silico spectroscopic analysis of As (10 mg/L) in the pH range 3–8 obtained with the spectroscopic program Visual MINTEQ ver. 3.1 under the following conditions: deionised water, 23 °C (**D**).

To investigate the effect of competition of other ions on the sorption process of As (10 mg/L), we used solutions of PO_4^{3-} and Cl^- ions at concentrations of 5, 10 and 20 mg/L. From the experimental data obtained on the sorption capacity of BC and MgBC, we found that PO_4^{3-} had a significant effect on As sorption for both sorbents. At BC and 5 mg/L PO_4^{3-} concentrations, there was no significant change in Q_{eq} value, but at higher concentrations the effect became more pronounced. Increasing the concentration to 10 mg/L PO_4^{3-} caused the Q_{eq} capacity value to decrease by more than half. At a concentration of 20 mg/L, there was an equally significant

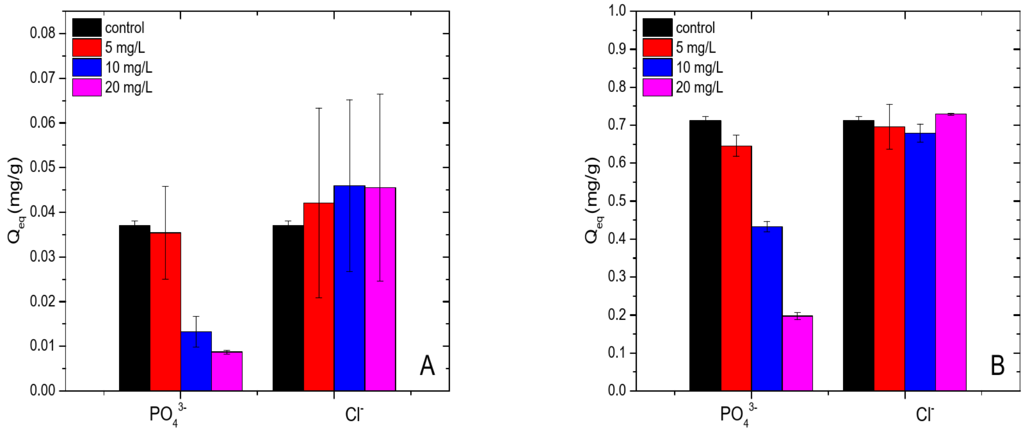

Fig. 7. Competitive effect of PO_4^{3-} and Cl^- on the As sorption process by BC (**A**) and MgBC (**B**) sorbents.

Desorption agent	Desorption efficiency (%)	
	BC	**MgBC**
HCl	50.01 ± 0.45	23.37 ± 3.51
NaOH	96.16 ± 0.86	97.69 ± 0.02
DV	25.66 ± 0.54	2.08 ± 0.85

Table 3. Regeneration of BC and MgBC sorbents by desorption reagents: deionized water (DV), NaOH (0.1 mol/L NaOH) and HCl (0.1 mol/L HCl) under desorption conditions: sorbent/desorbing agent ratio: 13.3 g/L, 23 °C, 24 h, 45 rpm.

decrease in sorbent capacity (Fig. 7A). For As sorption by MgBC-based sorbent and PO_4^{3-} concentrations, the Q_{eq} value decreased from 0.7 to 0.65 mg/g compared to the control. A concentration of 10 mg/L caused a more significant decrease in sorption capacity for As, to 0.45 mg/g. Subsequently, at a concentration of 20 mg/L, we observed a significant decrease in sorption capacity for As down to 0.2 mg/g (Fig. 7B). Based on our experimental data, we conclude that PO_4^{3-}ions significantly affect the sorption of As and with increasing concentration this effect increases for both sorbents. It is evident that phosphorus, as a chemical analogue of As, behaves similarly in aqueous solutions. The chemical speciation of As and P and the representation of similarly dissociated chemical forms, as well as the influence of solution pH, confirm that in the case of increased P concentration in solution, there is a significant reduction in the sorption efficiency of MgBC for As[32]. The basic characterization of the materials (Table 1) likewise confirmed that the BC material releases a higher concentration of phosphate and nitrate anions into the aqueous environment compared to MgBC, which only enhances the competence. On the other hand, this correlation refutes the possibility of the involvement of an ion-exchange mechanism between P and As anions bound in the BC structure. That the presence of phosphate anions significantly influences As sorption is also demonstrated by the work of Yan et al[25]., Lata et al[30]. and Huang et al[33].. In contrast, Cl^- ions did not have a significant effect on As sorption by both types of BC- and MgBC-based sorbents even at increasing concentrations (Fig. 7A, B).

To confirm the regenerability of BC- and MgBC-based sorbents, we studied 0.1 mol/L HCl, NaOH and deionized water as desorption agents. Table 3shows that the desorption reagent with the highest efficiency for both sorbents studied was 0.1 mol/L NaOH. The desorption efficiency of As at NaOH for both sorbents was more than 95% of the bound As. When 0.1 mol/L HCl was used as desorption reagent, the desorption efficiency for BC was 50% and for MgBC 23%. Deionised water was found to be the least effective desorption agent for both sorbents, with efficiency values of 25% for BC and approximately 2% for MgBC. Similar efficiency of alkaline desorption of biochar-bound As has been reported by several authors in their works[34–36].

As a final verification of the applicability of MgBC as a potential SPE column packing for the separation of As from real sample (liquid waste from experiments), we used 0.5 g of sorbent that was anchored between two layers of glass wool. Since from the previous results we found that the sorbent BC-based sorbent proves to be less effective for the separation and pre-concentration of As from aqueous solutions, we did not investigate its applicability in this experiment. The results obtained demonstrated the retention of As by a column packed with MgBC sorbent at a flow rate of 0.12 mL/s and given experimental conditions of 35 ± 2%. Higher efficiencies will be achieved when the sample flow rate through the column is reduced. This fact confirms the effectiveness of using the investigated material as SPE packing or sorbent for As pre-concentration and extraction procedures.

Conclusion

The application of solid pyrolysis products (biochar) as sorbents in preconcentration or extraction procedures and sample pretreatment methods represents a rather innovative approach in the use of these materials in non-aggregate routes. Both modified (MgBC) and unmodified biochar (BC) based sorbents were subjected to physicochemical characterization, which revealed significant differences in elemental, mineralogical as well as structural composition and surface morphology. Both materials were tested in a nested arrangement of sorption experiments as effective sorbents for the separation of As from aqueous solutions. The results obtained confirmed that MgBC exhibited 63-fold higher experimental sorption capacity Q_{eq} for As compared to BC. The sorption of As by BC and MgBC based sorbents is a pH and time dependent process with an optimum pH value of 5–6 and a contact time of 24 h. The sorption capacity of MgBC is dependent on the presence of phosphate anions in the solution, which eliminate As sorption. Both BC and MgBC sorbents proved to be well recoverable using 0.1 mol/L NaOH as desorption reagent (efficiency > than 95%). MgBC proved to be an equally effective cartridge of the SPE column with an As retention of 35 ± 2%. The obtained results indicate that pyrolysis products with appropriately chosen modification can compete with conventional stationary phases in preconcentration or purification columns.

Data availability

The datasets used and/or analysed during the current study available from the corresponding author on reasonable request.

Received: 11 September 2024; Accepted: 8 November 2024
Published online: 19 November 2024

References

1. Augusto, F., Hantao, L., Mogollón, N. G. S. & Braga, S. C. G.N. New materials and trends in sorbent for solid-phase extraction. *TRAC-Trend Anal. Chem.* **43**, 14–23 (2013).
2. Plotka-Wasylka, J., Szczepanska, N., de la Guardia, M. & Namiesnik, J. Modern trends in solid phase extraction: New sorbent media. *TRAC-Trend Anal. Chem.* **77**, 23–43 (2016).
3. Poole, C. F. New trends in solid-phase extraction. *TRAC-Trend Anal. Chem.* **22**, 362–373 (2003).
4. Lemos, V. A. et al. New materials for solid – phase extraction of trace elements. *Appl. Spectrosc. Rev.* **43**, 303–334 (2008).
5. Amalina, F. et al. Advanced techniques in the production of biochar from lignocellulosic biomass and environmental applications. *Clean. Mater.* **6**, 100137 (2022).
6. Bolan, N. et al. Zwieten, L.V. Multifunctional application of biochar beyond carbon storage. *Int. Mater. Rev.* **67**, 150–200 (2022).
7. Hagemann, N. et al. Activated carbon, biochar and charcoal: linkages and synergies across pyrogenic carbon´s ABCs. *Water*. **10**, 182 (2018).
8. Dieguez-Alonso, A. et al. Designing biochar properties through the blending of biomass feedstock with: Impact on oxyanions adsorption behavior. *Chemosphere*. **214**, 743–753 (2019).
9. Benis, Z. K., Damuchali, A. M., McPhedran, K. N. & Soltan, J. Treatment of aqueous arsenic – a review of biosorbent preparation methods. *J. Environ. Manage.* **273**, 111126 (2020).
10. Zhang, S. et al. Preparation of bamboo-derived magnetic biochar for solid-phase microextraction of fentanyls from urine. *J. Sep. Sci.* **45**, 1766–1773 (2022).
11. Ozdes, D. & Duran, C. Preparation of melon peel biochar/$CoFe_2O_4$ as a new adsorbent for the separation and preconcentration of Cu (II), cd (II) and pb (II) ions by solid-phase extraction in water and vegetable samples. *Environ. Monit. Assess.* **193**, 642 (2021).
12. Rovani, S., Medeiros, L. F., Lima, E. C. & Fernandes, A. N. Application of biochar from agro-industrial waste in solid-phase extraction for the determination of 17ß-estradiol from aqueous solutions. *Int. J. Environ. Sci. Tech.* **16**, 7623–7630 (2019).
13. Duran, C. & Ozdes, D. Application of magnetic Fe_3O_4 Alnus glutinosa Sawdust Biochar/SiO_2/CTAB as a new sorbent for magnetic solid phase extraction of heavy metals from fruit and water samples. *Int. J. Environ. An. Ch.* 16, 4857–4875 (2021).
14. Pipíška, M., Remenárová, L. & Environmentálne Biosorpcia toxických látok. 1. vyd. Trnava: UCM, 182 p. ISBN: 978-80-8105-531-7. (2014).
15. Langmuir, I. The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc.* **38**, 2221–2295 (1916).
16. Freundlich, H. M. F. Over the adsorption in solution. *J. Phys. Chem.* **57**, 385–471 (1906).
17. Sips, R. On the structure of a catalyst surface. *J. Chem. Phys.* **16** (5), 490–495 (1948).
18. Azizian, S. & Fallag, R. N. A new empirical rate equation for adsorption kinetics at solid/solution interface. *Appl. Surf. Sci.* 256, 5153–5156 (2010).
19. Jindo, K., Mizumoto, H., Sawada, Y., Sanchez-Monedero, M. A. & Sonoki, T. Physical and chemical characterization of biochar derived from different agricultural residues. *Biogeosciences*. 11, 6613–6621 (2014).
20. Li, H. et al. Mechanisms of metal sorption by biochars: biochar characteristics and modifications. *Chemosphere*. **178**, 466–478 (2017).
21. Saleh, M. E. & Hedia, R. M. R. Mg-modified sugarcane bagasse biochar for dual removal of ammonium and phosphate ions from aqueous solutions. *Alex Sci. Ex. J.* **39**, 74–91 (2018).
22. Singh, S. et al. Current advancement and future prospect of biosorbents for bioremediation. *Sci. Total Environ.* **709**, 135895 (2019).
23. Frišták, V. et al. Preparation and characterization of novel magnesium composite/walnut shell-derived biochar for as and P sorption from aqueous solutions. *Agriculture*. **11**, 714 (2021).
24. Ahmad, Z. et al. Removal of Cu(II), Cd(II) and Pb(II) ions from aqueous solutions by biochars derived from potassium-rich biomass. *J Clean Prod.* 180, 437–449 (2018).
25. Yan, J., Xue, Y., Long, L., Zeng, Y. & Hu, X. Adsorption removal of as (V) by crawfish shell biochar: batch and column tests. *Environ. Sci. Pollut Res. Int.* **25**, 34674–34683 (2018).
26. Zhu, S., Qu, T., Irshad, M. K. & Shang, J. Simultaneous removal od Cd (II) and As (III) from co-contaminated aqueous solution by α-FeOOH modified biochar. *Biochar* 2, 81–92 (2020).
27. Van Vihn, N., Zafar, M., K Behera, S. & S Park, H. Arsenic (III) removal from aqueous solution by raw and zinc-loaded pine cone biochar: equilibrium, kinetics and termodynamics studies. *Int. J. Environ. Sci. Tech.* **12**, 1283–1294 (2014).
28. Wang, S. et al. Manganese oxide-modified biochars: preparation, characterization, and sorption of arsenate and lead. *Bioresour, Technol.* 181, 13–17 (2015).
29. Xia, D. et al. $ZnCl_2$ – activated biochar from biogas residue facilitates aqueous as (III) removal. *Appl. Surf. Sci.* **377**, 361–369 (2016).
30. Lata, S., Prabhakar, R., Adak, A. & Samadder, S. R. As (V) removal using biochar produced from an agricultural waste and prediction of removal efficiency using multiple regression analysis. *Envriron Sci. Pollut R Int.* **26**, 32175–32188 (2019).

31. Rahman, H. L., Erdem, H., Sahin, M. & Erdem, M. Iron-incorporated activated carbon synthesis from biomass mixture for enhanced arsenic adsorption. *Water Air Soil. Poll.* **167**, 6 (2020).
32. Micháleková-Richveisová, B. et al. Iron-impregnated biochars as effective phosphate sorption materials. *Environ. Sci. Pollut Res. Int.* **24**, 463–475 (2017).
33. Huang, Y. et al. Efficient oxidation and adsorption of as (III) and as (V) in water using a Fenton-like reagent, (ferrihydrite)-loaded biochar. *Sci. Total Environ.* **715**, 136957 (2020).
34. Niazi, N. K. et al. Arsenic removal by Japanese oak wood biochar in aqueous solutions and well water: investigating arsenic fate using integrated spectroscopic and microscopic techniques. *Sci. Total Environ.* **621**, 1642–1651 (2018).
35. He, R. et al. Synthesis and characterization of an iron-impregnated biochar for aqueous arsenic removal. *Sci. Total Environ.* **612**, 1177–1186 (2018).
36. Amen, R. et al. Rinklebe, J. A critical review on arsenic removal from water using biochar-based sorbents: the significance of modification and redox reactions. *Chem. Eng. J.* **396**, 125195 (2020).

Acknowledgements
This work was funded by Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic, project number VEGA1/0399/24 and Faculty of Education of Trnava university in Trnava - project number B5/2024.

Author contributions
V.F., M.P., D.H.L. , E.M.J: established the idea, created experimental design, wrote the first draf , A.R.Z., V.F., D.H.L.: sampled and prepared materials L.Ď., I.Č., V. F., K. B., L. P., E.M.J : realized sorption and characterization experiments V. F., M.P : founded the research ideaV. F., L.P., K.B., E.M.J., M.P.: reviewed manuscript.

Declarations

Competing interests
The authors declare no competing interests.

Additional information
Correspondence and requests for materials should be addressed to V.F.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.