

## Modification of tea biochar with Mg, Fe, Mn and Al salts for efficient sorption of $\text{PO}_4^{3-}$ and $\text{Cd}^{2+}$ from aqueous solutions

Gökçen Akgül, Tuğba Bolat Maden, Elena Diaz and Eduardo Moreno Jiménez

### ABSTRACT

There is a requirement to provide more efficient, sensitive, low-cost materials for remediation of contaminated water. Biochar as a sorbent is an effective and low-cost material to remove contaminants in water but its adsorption properties can be improved by impregnation of metals on the surface. In this study, a biochar derived from industrial tea waste was modified with Mg, Fe, Mn and Al salts to create different composites, which were tested for  $\text{PO}_4^{3-}$  and  $\text{Cd}^{2+}$  sorption. The modifications created biochars with the (hydr)oxides of each metal and changed the characterization parameters and surface functionality.  $\text{Cd}^{2+}$  was efficiently removed by all the materials even at high  $\text{Cd}^{2+}$  loadings in the water ( $100 \text{ mg Cd}^{2+} \text{ L}^{-1}$ ), the biochar with Mg being the most efficient in  $\text{Cd}^{2+}$  removal. The biochar with Mg also achieved the best sorption of  $\text{PO}_4^{3-}$ , sorbing up to 30% at  $20 \text{ mg PO}_4^{3-} \text{ L}^{-1}$ . Tea waste biochar can be modified with metal salts to enhance inorganic pollutant removal from waters, especially with Mg salts.

**Key words** | adsorption, biochar,  $\text{Cd}^{2+}$ , metal impregnation,  $\text{PO}_4^{3-}$ , tea waste

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### INTRODUCTION

The world faces an increasing number of global threats and environmental problems, such as climate change, scarcity of water and water pollution. Water and agricultural resources, in particular, are under growing pressure as demands for food and fresh water increase with increasing world population (Mukheibir 2010). New threats include the challenges of climate change, which are likely to alter both water availability and agricultural water demands as well.

Managing and solving water contamination problems are now vital to maintain health, grow food, manage the environment, create jobs and even generate energy. Wastewater containing various pollutants has been treated with

traditional methods such as precipitation, coagulation, ion exchange, membrane separation, reverse osmosis, extraction and electrochemical methods (Muga & Mihelcic 2008). These methods require expensive solvents, advanced technologies or complicated measurement and monitoring systems (Hashim *et al.* 2011). Toxicity of additives or sludge is another difficulty for the traditional methods.

There are still challenges to improve more efficient and low-cost technologies for remediation of contaminated water. The task can be achieved by innovative methods and technologies in many different approaches. One such approach is use of biochar (BC) for environmental management (Ahmad *et al.* 2014; Tan *et al.* 2015; Sizmur *et al.* 2017).

BC is a carbonaceous material derived from biomass pyrolysis that stands out as a sustainable material. Because of its properties, similar to activated carbon (AC), it has

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recently been used as a sorbent material to reduce contaminants such as inorganic species, organics or pesticides (Ahmad *et al.* 2014). Pollutants in water can be adsorbed and retained by the efficient adsorption properties of BC (Ahmad *et al.* 2014; Mohan *et al.* 2014b; Rajapaksha *et al.* 2014; Tan *et al.* 2015). Elaigwu *et al.* (2014) reported that BC prepared from pyrolysis of *Prosopis africana* shell could be used to adsorb toxic  $Pb^{2+}$  and  $Cd^{2+}$  from aqueous systems. Han *et al.* (2013) investigated the  $Zn^{2+}$ ,  $Cu^{2+}$  and phenol adsorptive capacities of BCs derived from three different biomass sources. The adsorption properties of BC samples were as high as for AC and it was stated that BCs are suitable for removal of heavy metals and phenolic compounds from water effluent. However, BC failed to retain oxyanions (P, Cr or As) due to the predominantly negatively charged surface of BC (Tripathi *et al.* 2016). However, the surface can be modified to improve adsorption capabilities by various methods such as metal impregnation (Sizmur *et al.* 2017) or irradiation (Wang *et al.* 2017).

BC is a generic term and its characteristics are very variable depending on the composition of the source biomass and pyrolysis conditions (Mohan *et al.* 2014a; Tan *et al.* 2015). Every BC has its own characteristics for adsorption (Yao *et al.* 2011; Zhang *et al.* 2013b; Wang *et al.* 2015b; Goswami *et al.* 2016; Jung *et al.* 2016). Numerous studies can be found on adsorption of pollutants by BC and characteristics of BC derived from various biomass resources (Jung *et al.* 2015a; Ahmed *et al.* 2016; Jung & Ahn 2016; Trakal *et al.* 2016; Sizmur *et al.* 2017). The main properties providing advantages for adsorption by BC can be summarized as high surface area, effective surface functionality, negatively charged surface and ion exchange ability. Although BC is such a great material for removal of contaminants, its properties could be improved to make better use of it. Impregnation of metals on the BC surface is one of the methods that improve the adsorption ability and selectivity by modifying the surface. Rajapaksha *et al.* (2016) call this type of BC 'engineered biochar' and suggested it provides better solutions for recovery of contaminants and better separations.

Industrial tea waste is an abundant material, as tea is widely grown. Currently, tea waste is disposed of by inefficient incineration, which causes air pollution. These wastes are suitable for evaluation as BC and composites for use in removal of  $Cd^{2+}$  and  $PO_4^{3-}$  pollutants from water

effluents. Anionic  $PO_4^{3-}$  and cationic  $Cd^{2+}$  are common pollutants emerging as a result of industrial activities to produce commercial products such as NiCd batteries, plating, pigments, plastics and fertilizers. Excessive amount of  $PO_4^{3-}$  and  $Cd^{2+}$  in the environment can cause harmful blooms of cyanobacteria in water, which leads to scarcity of oxygen in water and kidney problems when taken up by humans via food chains.

Studies determining the adsorption capacities of BC and BC composites based on tea waste biomass are limited. In the present study, the characteristics of BC from industrial tea waste and metal composites (Mg, Fe, Mn, Al, which are effective for the formation of oxy(ogenated) groups) were determined, and their  $Cd^{2+}$  and  $PO_4^{3-}$  adsorption capacities are discussed in detail.

## METHODS

### Preparation and characterizations of BC samples

The BC was produced by a batch-type rotating oven (Carbolite, HRT 11/150) with a cylindrical quartz reactor having around 3 L total volume. The biomass resource tea waste is the end product of tea processing, mostly comprised of the separated waste tea leaves from various stages of production and the accumulation of dust and stalks. The tea waste was provided by a tea plant located in Rize-Turkey (the Black Sea Region), in the form of straw (<2.36 mm) and it was used for BC production without any grinding or pre-treatments. The oven temperature was set to 500 °C with 10 °C/min heating rate and experiments were performed under  $N_2$  atmosphere with 1 L/min flow rate. The retention time was 1.5 h at the desired temperature. The BC production yield was around 30–33% at 500 °C. The BC sample obtained was crushed in a mortar.

The metal impregnation of the BC was performed by treatment with salts of  $MgCl_2 \cdot 6H_2O$  (Panreac, 98%),  $Fe(NO_3)_3 \cdot 9H_2O$  (Panreac, 98%),  $KMnO_4$  (Panreac, 98%) and  $Al(NO_3)_3 \cdot 9H_2O$  (Merck, >95%) with the metal impregnation ratios of 8%, 8%, 6% and 5%, respectively. The salt solutions were prepared in water to a volume that was matched to the BC water-holding capacity (1.5–1.8 ml). The BC was watered with the corresponding salt solution in small amounts with homogenization steps until all the

solution had been added to the BC. The mixture was agitated every 15 min for 2 h then dried at 100 °C overnight. The metal-salt-treated and dried BC samples were calcined at 300 °C with 3 °C/min heating rate and 3 h dwelling time in the oven under air atmosphere to allow formation of metal oxide on the BC surface by decomposition. The metal-impregnated BC samples were labelled as BC-Mg, BC-Fe, BC-Mn and BC-Al according to the metal that was in each solution.

The tea waste biomass and BC samples were characterized by various methods: elemental analysis according to ASTM D3176-89 (LECO CHNS 932); infrared spectroscopy (Fourier-transform infrared spectroscopy (FTIR) with coupled attenuated total reflectance (Perkin Elmer Spectrum 100), and the surface morphology was scanned by a scanning electron microscope (SEM) (JEOL/JSM-6610). The formation of oxides for all samples was checked with SEM-energy dispersive X-ray spectroscopy (EDS) analysis as well. The specific surface areas were determined by Brunauer–Emmett–Teller (BET) analysis (Quantachrome Autosorb 1C and Quantachrome ASiQwin™). The cellulose, hemicellulose and lignin content of tea waste biomass on a dry basis were determined according to Technical Association of Pulp and Paper Industries standards, and mineral content by X-ray fluorescence (PANalytical, EPSILON 5 Model X-ray fluorescence spectrometer). Proximate ash and volatile matter analyses were performed according to ASTM D3174-04 and ASTM D3175-89, respectively.

The leaching of metals from each impregnated material was determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Icap 6500 Duo Thermo). The pH values of the BC samples were determined for 0.01 and 0.1 g/10 ml BC–water mixtures. The water solutions were stirred overnight and filtered. The required values were determined by Metrohm-914 type pH/conductometer.

A commercial AC was also used as a sorbent to compare the adsorption capacities (Carbomix, <http://www.cabot-corp.com/solutions/products-plus/activated-carbon>).

### Batch sorption experiments

Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (98%) and KH<sub>2</sub>PO<sub>4</sub> (>98%) supplied by Sigma-Aldrich were used as adsorbates in the adsorption studies. Stock solutions of 500 mg Cd<sup>2+</sup>/L and

1,000 mg PO<sub>4</sub><sup>3-</sup>/L were prepared in a volumetric flask and diluted with double distilled water to the required concentrations in the range 10–100 mg/L. The experiments were carried out in 50 ml Erlenmeyer flasks. In each test, 0.01 g BC adsorbent was added to 10 ml of solution at the required concentration. The flasks were placed on an orbital shaker (Heidolph Unimax 1010) and shaken at room temperature at 150 rpm for 24 h. After adsorption, the mixtures were filtered with 0.45 µm syringe filters. The Cd<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> concentrations in the solutions were determined by ICP-OES (Perkin Elmer Optical Emission Spectrometer Optima 7000 DV) and UV-visible spectrophotometer (Hach Lange DR 3900, at 430 nm, in the presence of ammonium molybdate/vanadate standards), respectively. The experiments were performed in triplicate.

The amount of Cd and P uptake by adsorbents was calculated by Equation (1).

$$R \% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

where *R%* is the removal percentage, *C<sub>0</sub>* is the initial metal concentration (mg L<sup>-1</sup>), *C<sub>e</sub>* is the adsorbate concentration (mg L<sup>-1</sup>) remaining in the solution at a given time.

## RESULTS AND DISCUSSION

### Characterization of BC and composites

The results of proximate and ultimate analyses of the samples are given in Table 1. The moisture and ash contents and volatile matter of tea waste biomass were determined as 7.20%, 3.74% and 70.00%, respectively. BC composites had less than 1% moisture content.

Carbonization was achieved by pyrolysis, which raised the C content from 45% for tea waste to 70% for BC. The feedstock and consequently BC samples contain small amounts of sulphur. The N content was increased around 1–1.5% when the metal nitrate salts were used for preparing BC-metal composites, which indicates possible interactions between nitrate and tea BC on the surface.

The surface areas of the adsorbents are given in Table 1. As expected, the AC has the highest surface area of

**Table 1** | Ultimate and proximate properties of tea waste biomass (TW), biochar (BC), composites (BC-Mg, BC-Fe, BC-Mn, BC-Al) and a commercial AC

	TW	BC	BC-Mg	BC-Fe	BC-Mn	BC-Al	AC
Proximate analysis (wt.%, as received)							
Moisture	7.20	1.5	<1.0	<1.0	<1.0	<1.0	<1.0
Volatile matter	70.29						
Ash	3.74						
Ultimate analysis (wt.%, dry basis)							
C	45.4	69.6	37.4	41.3	28.4	40.2	75.8
H	5.7	3.3	3.3	1.7	1.4	2.0	1.6
N	2.9	2.9	2.4	4.0	2.0	4.3	1.1
O <sup>a</sup>	46.0	24.2	48.9	45.0	62.2	48.5	21.5
S	<1	<1	<1	<1	<1	<1	<1
O/C (S ignored)	1.01	0.35	1.31	1.09	2.199	1.21	0.28
Surface area (m <sup>2</sup> /g)	12.7	5.711	7.082	11.418	3.785	2.927	1,108.0

<sup>a</sup>The oxygen content was determined by difference [100% – (C% + H% + N%) - (metal content)].

1,108 m<sup>2</sup>/g. The surface areas of tea waste biomass, BC and composites were much smaller, around 3–13 m<sup>2</sup>/g. Generally, carbonization of biomass or metal impregnation of BC decreased the surface area, possibly because pyrolysis collapses the structure and salt oxides blocks. However, Mg and Fe impregnation of BC increased the surface area slightly, which could be the result of formation of different crystal structure or magnetite properties.

Tea plant material mainly consists of cellulose (13.5%), hemicellulose (34.2%) and lignin (38.7%), respectively. The mineral composition of tea waste is shown in Table 2 with the content of around 15%. The main minerals are K, Ca, Mn and P.

Converting tea waste biomass to BC and metal impregnation change the surface morphology. Figure 1(a) shows

**Table 2** | Mineral content of raw tea waste

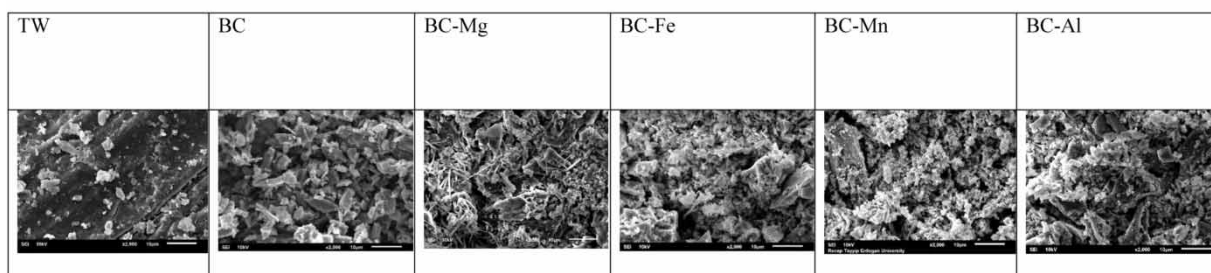
Compound	Content (wt%)
K <sub>2</sub> O	8.23
CaO	3.23
MgO	0.09
Al <sub>2</sub> O <sub>3</sub>	1.15
P <sub>2</sub> O <sub>5</sub>	0.81
MnO	1.01
Fe <sub>2</sub> O <sub>3</sub>	0.48
Cl	0.22

the SEM pictures of the samples (10 kV, ×2,000, 10 μm). Carbonization of tea waste biomass breaks up the structure to smaller particles at first, while treating BC with metal salts and subsequent calcination coats the BC matrix with metal oxides. These coated forms are assumed to be oxide forms of salts, such as MgO, MnO<sub>x</sub>, Fe<sub>x</sub>O<sub>y</sub> and Al<sub>x</sub>O<sub>y</sub> (Zhang *et al.* 2012; Jung & Ahn 2016; Thines *et al.* 2017). Figure 1(b) shows a sample EDS analysis for BC-Fe. The intensity of the oxygen peaks increased for all composite BC samples.

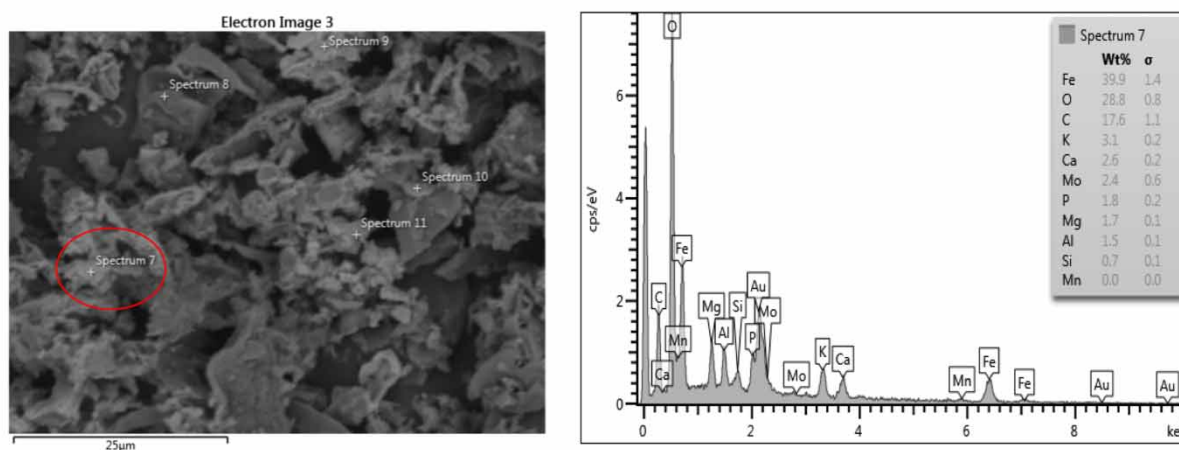
Elemental analyses given in Table 1 confirm that the O/C ratios are higher for impregnated BC samples, which could be the result of oxidation of the surface. The crystalline needle structure of MgO observed by SEM corresponds to reported structures (Li *et al.* 2017). SEM pictures also show that BC samples have a more fibrous structure than AC. Although the particles of AC seem larger than BC and composites, AC has a more porous structure.

Understanding the physicochemical properties of different BC composite samples is crucial and mostly related to surface functionality. Figure 2 shows the FTIR results of the samples. Since tea leaves mainly consist of cellulose, hemicelluloses, lignin, tannin and flavonoid molecules (phenolic compounds), the dominant functional groups are mainly phenolic hydroxyls and carboxylates: OH (3,600–3,200 cm<sup>-1</sup>), aliphatic C–H groups (2,956–2,856 cm<sup>-1</sup>), C = O and C = C (1,600–1,400 cm<sup>-1</sup>), NO<sub>2</sub> (1,320–1,370 cm<sup>-1</sup>), C–O (1,200–1,300 cm<sup>-1</sup>), aromatic C–H stretching (900–700 cm<sup>-1</sup>) and

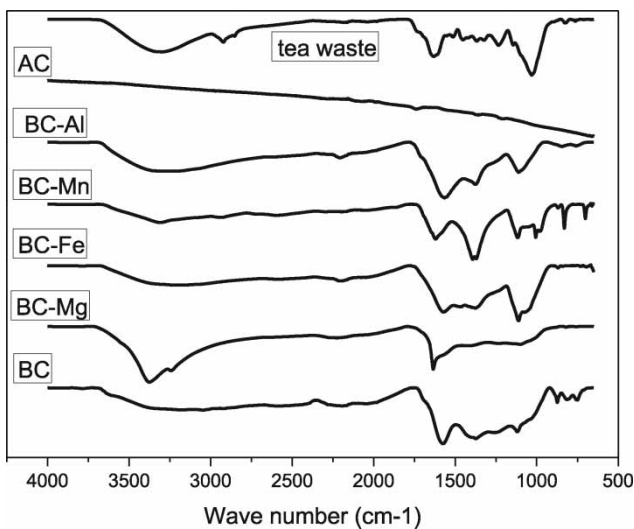
(a)



(b)



**Figure 1** | (a) SEM images of the samples (upper); (b) SEM-EDS images of BC-Fe (lower).



**Figure 2** | FTIR analyses of the samples.

C–C stretching ( $<700 \text{ cm}^{-1}$ ). New peaks observed, especially for BC-Mn around  $600 \text{ cm}^{-1}$ , may be due to the stretching of the Mn–O bond. The stronger OH band of BC-Mg could be a

result of stronger O–H stretching and different crystalline structure of the oxide. The identical stretching for Mg–O–Mg at around  $850 \text{ cm}^{-1}$  was swallowed by the other peaks. The FTIR spectrum for AC seems very flat, which could mean that there are fewer specific functional groups on the surface than BC and composites. Metal leaching to the water was observed only for the BC-Mg sample, as around 2%.

In summary, BC and metal-impregnated composites are rich in functional groups on the surface, unlike the AC. Metal impregnation of the BC coats the surface with oxides in different crystalline structures. The surface areas of BC and composites are much smaller than that of AC and are less porous.

### Adsorption of $\text{PO}_4^{3-}$ and $\text{Cd}^{2+}$ from aqueous solutions by BC and metal composites

The adsorption of anionic  $\text{PO}_4^{3-}$  and cationic  $\text{Cd}^{2+}$  by BC, composites and AC was determined. The results are

shown in Figures 3 and 4 for  $\text{PO}_4^{3-}$  and  $\text{Cd}^{2+}$  removal, respectively.

The removal of anionic  $\text{PO}_4^{3-}$  only occurred with BC and BC-Mg at around 25% and 30% for 10 and 20 mg  $\text{PO}_4^{3-} \text{L}^{-1}$ , respectively. All materials were more successful for removing cationic  $\text{Cd}^{2+}$  from water even at high concentrations (100 mg  $\text{Cd}^{2+}/\text{L}$ ). AC was a less effective sorbent for both ions than BC and composites. Furthermore, all metal-impregnated samples were much more successful than BC. The fluctuations of some isotherms may be attributed to biomass hysteresis characteristics.

At first glance, the results indicate that surface functionality of sorbents is a much more effective parameter than

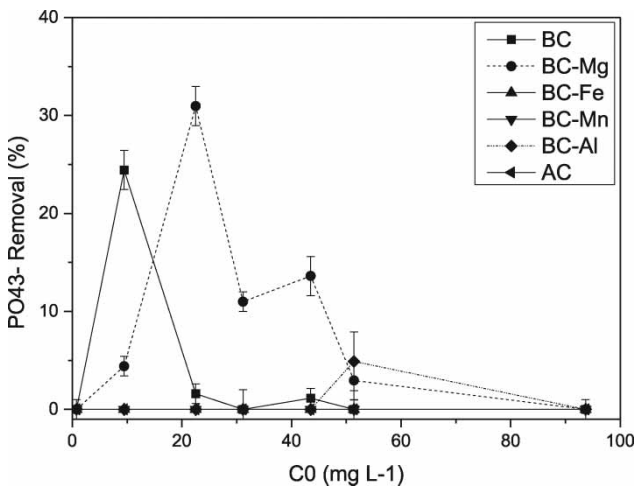


Figure 3 |  $\text{PO}_4^{3-}$  removal by biochar (BC), composites and AC.

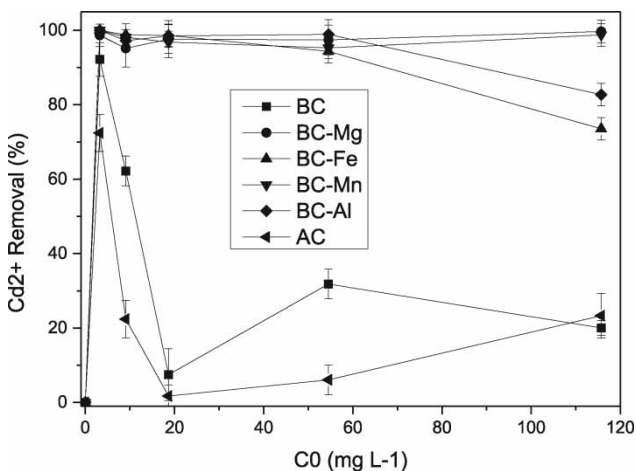


Figure 4 |  $\text{Cd}^{2+}$  removal by biochar (BC), composites and AC.

surface area for both anionic and cationic ion removal since removal by highly porous AC was noticeably less than by BC and composites. Therefore, the dominant adsorption mechanism could possibly be interactions of ions with surface functional groups, which would promote the effective removal of pollutants  $\text{PO}_4^{3-}$  and  $\text{Cd}^{2+}$ .

Metal impregnation of BC is generally used to modify the surface to enhance the surface functionality by forming new bonding sites (Hua *et al.* 2012; Khajeh *et al.* 2013). BC has desirable properties, such as chemical activity, porosity and adsorption ability, allowing it to be functionalized by covalent linking of metal oxides, which are deposited on the surface. Metal oxide deposited on the BC surface becomes more attractive for both anionic and cationic molecules by providing specific affinities. Generally, metal-impregnated BC containing positive sites and improved oxidized surface would be attractive for anionic ions. Zhang *et al.* (2012) reported that MgO-impregnated BC derived from a pair of different biomass feedstocks showed excellent removal efficiencies of phosphate in water. They showed that impregnation of Mg caused formation of nano-sized MgO grains on the BC surface. This method increased the surface area and micro-porosity of BC as well. In the present study, surface area increase from 5.7 to 7.1  $\text{m}^2/\text{g}$  was observed for BC-Mg. However, this value is in the experimental error range. Jung & Ahn (2016) reported that  $\text{PO}_4^{3-}$  removal capacity of MgO-impregnated BC is higher than raw BC or  $\text{MgCl}_2$  BC composite due to the stronger interaction between the phosphate and MgO BC. The removal mechanism was also explained as ion exchange and precipitation at lower and higher  $\text{PO}_4^{3-}$  concentrations, respectively.

Fe-, Mn- and Al-impregnated BC samples could provide positive surfaces for better  $\text{PO}_4^{3-}$  adsorption, but the results of the present study show that they are less effective than untreated BC. Since BC and BC-Mg are able to remove  $\text{PO}_4^{3-}$ , interactions other than with the oxidized surface should play a role in the adsorption process.

Micháleková-Richveisová *et al.* (2017) stated that pH plays an important role for adsorption of  $\text{PO}_4^{3-}$  by Fe/BC composites since adsorption could be achieved only at pHs around 5, which is explained by attraction of  $\text{PO}_4^{3-}$  to the positively charged surface. In the present study, by contrast,  $\text{PO}_4^{3-}$  adsorption by BC and BC-Mg was successful at pH around 9–10.

**Table 3** | Cd<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> adsorption capacities demonstrated in various studies

BC feedstock	Pyrolysis method	Activation/modification	Cd removal (mg g <sup>-1</sup> )	P removal (mg g <sup>-1</sup> )	Reference
Switch	Hydrothermal carbonization	KOH	34	–	Regmi <i>et al.</i> (2012)
Hickory	Pyrolysis	–	28.1	–	Wang <i>et al.</i> (2015a)
<i>Canna indica</i>	Pyrolysis	HCl	188.8	–	Cui <i>et al.</i> (2016)
<i>Ipomoea fistulosa</i>	Pyrolysis	KOH	72.43	–	Goswami <i>et al.</i> (2016)
Oak wood	Pyrolysis	–	0.37	–	Mohan <i>et al.</i> (2007)
Oak bark			5.40		
Sugar beet tailings	Pyrolysis	MgO	–	835	Zhang <i>et al.</i> (2012)
Corn cob	Pyrolysis	MgO/CaO	–	326.63	Fang <i>et al.</i> (2015)
Bamboo	Pyrolysis	Mg/Al or Mg/Fe loaded layered double hydroxide	–	172	Wan <i>et al.</i> (2017)
Cotton wood	Pyrolysis	Mg/Al loaded layered double hydroxide	–	410	Zhang <i>et al.</i> (2013a)
Marine macroalgae	Electrochemical modification and pyrolysis	Periclase MgO	–	620.66	Jung & Ahn (2016)
Cotton stalks	Pyrolysis	Treated with MgCl <sub>2</sub> before pyrolysis	–	129.90	Yu <i>et al.</i> (2016)
Wood chips	Pyrolysis	Fe(OH) <sub>3</sub>	–	3.2	Micháleková-Richveisová <i>et al.</i> (2017)
Cotton stalk	Chemical precipitation	FeO, Fe <sub>2</sub> O <sub>3</sub>	–	0.963	Jing <i>et al.</i> (2015)
Water hyacinth	Pyrolysis	Fe <sub>3</sub> O <sub>4</sub> and Fe <sub>2</sub> O <sub>3</sub>	–	5.07	Cai <i>et al.</i> (2017)
Cottonwood	Pyrolysis	AlOOH	–	135	Zhang & Gao (2013)
<i>Laminaria japonica</i>	Electro-modification	Al	–	345–460	Jung <i>et al.</i> (2016)
<i>Laminaria japonica</i>	Electro-modification	Mg-Al	–	887	Jung <i>et al.</i> (2015b)
Oak wood	Chemical precipitation	Fe <sup>2+</sup> /Fe <sup>3+</sup> , NaOH	2.87	–	Mohan <i>et al.</i> (2007)
Oak bark			7.40		
Pine bark	Pyrolysis	CoFe <sub>2</sub> O <sub>4</sub>	17.8	–	Reddy & Lee (2014)
Nut shield	microwave	Fe <sub>2</sub> O <sub>3</sub>	50.6	–	Trakal <i>et al.</i> (2016)
Wheat straw			75.3		
Grape stalk			64.1		
Grape husk			38.3		
Plum stone			47.0		
Hickory wood	Pyrolysis	MnO <sub>x</sub> (KMnO <sub>4</sub> )	28.1	–	Wang <i>et al.</i> (2015a)
Rape straw	Pyrolysis	MnO <sub>x</sub> (KMnO <sub>4</sub> )	81.1	–	Li <i>et al.</i> (2017)
Tea waste	Pyrolysis	- (BC)	20	24	Present study
		MgO	~100	30	
		Fe <sub>x</sub> O <sub>y</sub>	74	0	
		MnO <sub>x</sub>	~100	0	
		Al <sub>x</sub> O <sub>y</sub>	83	5	
		Commercial AC	23	0	

BC, composites and AC sorbents were successful in removing the cationic  $\text{Cd}^{2+}$  ion. Various mechanisms such as ion exchange, precipitation, porosity, chemical-physical-magnetite interactions should be effective and compete with each other.

Reddy & Lee (2014) demonstrated that after loading magnetic  $\text{CoFe}_2\text{O}_4$  on to pine bark BC, the OH functional groups predominate and they are able to provide coordination with  $\text{Cd}^{2+}$  ions on the surface and result in better adsorption. Li et al. (2017) concluded that  $\text{MnO}_x$ -modified rape straw BC shows a better affinity than unmodified, Fe-modified or NaOH-activated, due to creation of new oxygen-containing groups forming adsorption sites on the surface.

In the present study, retention of anions and cations on BC could be enhanced by modifications of the BC surface with (hydr)oxides of metals as described by Gomes-Eyles et al. (2013) and Beesley et al. (2011). The interactions between BC-Mg and BC-Mn seem stronger than other BCs even at high  $\text{Cd}^{2+}$  ion concentrations. Similar to  $\text{PO}_4^{3-}$  adsorption,  $\text{Cd}^{2+}$  adsorption should be a result of interactions of  $\text{Cd}^{2+}$  and surface functional groups containing oxygen or metal by complexation rather than surface area or particle size. In Table 3, some published studies of  $\text{PO}_4^{3-}$  and  $\text{Cd}^{2+}$  adsorption capacities by BC composites obtained from isotherms are summarized. It is notable that every BC from various feedstocks, and made by different pyrolysis methods, have different adsorption capacities even for the same anion or cation or metal loading.

## CONCLUSIONS

The anionic  $\text{PO}_4^{3-}$  and cationic  $\text{Cd}^{2+}$  ion removal capacities of BC derived from tea waste biomass and metal-impregnated composites were determined. The results showed that BC and metal-impregnated composites are an effective and low-cost material to remove  $\text{PO}_4^{3-}$  and  $\text{Cd}^{2+}$ . Metal impregnation of BC improved the adsorption properties by creating (hydr)oxides of each metal impregnated onto the surface. BC- and metal-impregnated composites are rich in functional groups on the surface, so the functionality plays a more effective role than porosity for removing the pollutants  $\text{PO}_4^{3-}$  and  $\text{Cd}^{2+}$ . Mg-impregnated BC is the most efficient composite among those impregnated with Fe, Mn

and Al in  $\text{Cd}^{2+}$  reduction and also the sorption of  $\text{PO}_4^{3-}$  by possible different interactions than those with the oxidized surface. Tea waste BC can be modified with metal salts to enhance inorganic pollutant removal from waters, especially with Mg salts.

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