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Review

A state of the art review on phosphate removal from water by biochars

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ABSTRACT

In the last decade, biochar (BC) has attracted significant attention for the removal of pollutants from aqueous solutions. Biochar exhibits many distinctive characteristics that make it an attractive adsorbent due to its availability, low manufacturing cost and compelling surface properties. This review presents a comprehensive summary of BC's application in phosphate remediation. Adsorption isotherm, kinetics, experimental conditions and the effect of different adsorption parameters on phosphate removal are outlined. The adsorption mechanisms, effect of coexisting ions, desorption studies and reuse of exhausted BCs are also considered. The results demonstrate that unmodified BCs possess low phosphate sorption capacity with the exception of BCs with high minerals content. As such, engineered BCs by decoration with different elements have been shown to alter the surface characteristics of the adsorbents such as surface charge, surface area, pore diameter, pore volume and the surface functional groups. Therefore, the phosphate sorption capacity of modified BCs has been significantly improved compared to unmodified adsorbents. Magnesium, aluminum, calcium and lanthanum were of significant interests for BC decoration due to their high affinity toward phosphate ions. Iron has been also widely used in BC composites for increasing the adsorption capacity of phosphate, in addition to providing an opportunity for magnetic recovery of the adsorbent. Based on this review, future research for BC applications in terms of phosphate removal is also discussed.

1. Introduction

Phosphate is the main cause of eutrophication, which poses various risks to humans, animals and plants [1]. For several years, the existence of phosphate in the different water resources has been an expanding phenomenon from different sources, yet the two most high risk sources are; i) the presence of phosphate in sewage waters and phosphate traces in the treated sewage effluent (TSE), ii) the runoff from agricultural lands due to phosphate fertilizers spreading and dissolution in rain water and consequently the discharge of phosphate into rivers and other surface and underground water resources [2]. The issue of phosphate from fertilizer runoff has been shown to cause extreme algal growth and microcystins (MCs) production in surface waters [3,4]. Further problems arise from algae transportation into the water tanks, which can lead to a blockage in the turbines and water pipes in reservoir pumping and

power generating plants [5]. The presence of toxic red algae and dinoflagellates on the seashore areas has caused the loss of millions of dollars' worth of fish farming stocks, thus resulting in more economic upheavals. There is an increasing global environmental concern about MCs growth caused by phosphate eutrophication and algal blooms. MCs represent a class of toxins that can accumulate in an aquatic environment, leading to decreased aquatic diversity and problems in fish farming [6]. MCs can also be transported to drinking water and enter the food chain through irrigation and can hence affect human health [7].

In the last decade, a substantial amount of research has been directed towards the utilization of TSE water for agricultural applications, primarily attributed to the water stress security crisis, forecasts of food security deficiencies and increasing phosphate nutrient concentration [8,9]. Replenishing the lands by phosphate waste, whether created by TSE or fertilizers run-off contributes towards "recycling and reuse"

Abbreviations: Q_m , maximum adsorption capacity; F, Freundlich; L, Langmuir; L-F, Langmuir-Freundlich; PFO, Pseudo first order; PSO, Pseudo second order.

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Table 1

Global demand of phosphate fertilizers and mine production of phosphate rocks. Source of data [20,21].

| Year | Global phosphate demand for fertilizer (million ton P_2O_5) | Global non-fertilizer phosphate demand (million ton P_2O_5) | Global mines production of phosphate rocks (million ton) |
|----------------------|--|--|--|
| 2015 | 41.74 | 3.52 | 241 |
| 2016 | 41.95 | 3.57 | 255 |
| 2017 | 43.20 | 3.62 | 269 |
| 2018 | 44.12 | 3.65 | 270 |
| 2019 | 45.01 | 3.69 | – |
| 2020 | 45.13 | 3.73 | – |
| 2023/2024 Projection | 49.60 | – | – |

activities that contribute towards sustainable development. Nevertheless, a challenge related to the variation of phosphate concentrations in TSE when directly applied has arisen, hence the phosphate dosage for lands may not be consistent. Accordingly, the adsorptive removal of phosphate from TSE and runoffs before its recovery and reuse is advantageous in order to monitor the application of the reclaimed phosphate [10]. The phosphate loaded biochar (BC) can be applied directly on lands with the dual benefit of soil quality enhancement by BC, coupled with the slow release of the phosphate nutrient from BC during irrigation thus providing better phosphate management and benefit to the crops [11].

Amongst the chemical, physical and biological methods used for removing phosphates from water; adsorption technology has proven to be effective for removing phosphates even at low concentrations [12]. Adsorption technology is also easy to operate as it requires a relatively simple design, and offers the possibility of adsorbent regeneration and normally produces low amounts of by-products [13,14]. Furthermore, phosphate is required for different living organisms and can be used in different applications, including in agriculture as a fertilizer. Notably, phosphate is a non-renewable natural resource. Therefore, during the last decade, research efforts have been focused on adsorbents with high capacity, in addition to the conditions for adsorbent regeneration to release the phosphates.

The demand for phosphate fertilizers is increasing annually by 1 to 2 percent. It is expected that the demand in 2023 will be approximately 50 million tons as illustrated in Table 1. Phosphate rocks are the main source of phosphate fertilizers and contains up to 35% of low grade to high grade quantities of phosphate (as P_2O_5) [15]. Table 1 also illustrates the increase in mine production of phosphate rock annually; 80–90% of this amount is consumed for the production of fertilizers [16]. Notably, current phosphate mining is associated with several environmental issues related to air, land and water pollution as well as the social aspects. Phosphate rock mining has led to rock desertification, landscape modification, loss of biodiversity, dust and air pollution, ground erosion, ore extraction, radioactive elements found in phosphate rock and their effect on human and other impacts [17]. Several reports indicate that this source of phosphate is depleting and can only meet the demand for phosphate fertilizers for a certain number of years [18]. Cardoll et al. [19] reported that for the efficient use of phosphate, 1/3 of the projected demand should be fulfilled through the efficient recovery of phosphate from human excreta, manure, food waste and mining waste as indicated in Fig. S1. Large amounts of phosphate are available in manure and human excreta, which are usually present in wastewater streams. Therefore, the adsorption of phosphate from wastewater will contribute to meeting the future demand for phosphate and consequently decrease the environmental impact of phosphate rock mining.

Several adsorbents have been employed for phosphate elimination from aqueous solutions such as, zeolites [22], polymeric adsorbents [23], porous silica [24], activated carbon [25] and clay minerals [24]. Amongst these adsorbents, activated carbon has been widely used for

phosphate removal due to its porous structure, stability and high surface area. However, many of the activated carbons often possess hydrophobic or very weak charged groups on their surface, and hence they demonstrated a poor phosphate adsorption capacity. In this regard, activated carbons were impregnated or modified with metal ions to improve their phosphate adsorption capacity [25,26]. Despite this, the search for cheaper adsorbents with higher phosphate capacity is still an ongoing research endeavor.

Biochar is a carbon rich material, produced by thermal processing of different types of biomass under limited oxygen supply conditions [27]. Although BC and activated carbon are made from similar materials and manufacturing methods, BC is manufactured at a lower temperature than the activated carbon, resulting in a price of BC that is 1/6 of the price of the commercial activated carbon [27,28]. In addition, and in spite of the modification of the materials for specific applications, the production of BC does not require the activation step [28]. However, producing BC or activated carbon relies mainly on the target for which the material was made. In the last decade, BC has attracted significant attention for the removal of organic and inorganic pollutants, along with soil fertility enhancement [29]. For pollutant removal, BC has been considered an important competitor adsorbent to the available adsorbents, mainly activated carbon, since it is cheaper and requires less energy for production [30]. Furthermore, the engineered BCs have resulted in comparable adsorption capacities to that of activated carbon [31]. BC also possesses unique properties such as high surface area, high porosity, availability of a wide range of feed-stocks, abundant oxygen functional groups, the ease of production and stable carbon structure [32]. In addition, the conversion of different kinds of biomass into a valuable BC supports the reduction of greenhouse gases and leads to the enhancement in the soil fertility, which accordingly decreases the environmental stress. A wide range of feedstocks have been used for BC fabrication including plant biomass, animal waste, sludge and marine microalgae [33]. The surface and chemical properties of the BC are highly affected by the type of the feedstock, production method, production temperature, heating rate and the residence time of heating [34]. BCs can be produced using different processes such as hydro-thermal carbonization, slow pyrolysis, fast pyrolysis and gasification. These topics have been discussed by Lehmann and Joseph in their recent book [35]. Several reviews have also reported the removal of phosphate from aqueous solutions [11,25,26,36–40]. However, the focus was not given to BCs, with the exception of carbon adsorbents as subsections in Bacelo et al. [25], Liu et al. [40] reviews. Vikrant et al. [11] reviewed some aspects of phosphate removal with BC in the studies published up to 2016, although, they did not discuss the adsorption thermodynamics, effect of coexisting ions and desorption processes.

The current study presents a critical and comprehensive review of the literature that has reported the adsorptive removal of phosphate by modified and unmodified BCs in the period of 2011 to 2020. A summary of the published data in terms of, BC preparation conditions, BC surface properties, adsorption experimental conditions, isotherms, kinetics, optimum pH and maximum adsorption capacity are presented. The effect of coexisting ions, adsorption thermodynamics, desorption analysis, the use of exhausted BCs and phosphate adsorption mechanisms are also discussed. Furthermore, the future aspects of phosphate removal by BCs is also highlighted.

2. Removal of phosphate by BC

Since Chen et al. [41] began removing phosphate using BC in 2011, in which scientific research to remove phosphate using BC and its composites has been increasing annually. This is mainly attributed to its low price, wide variety of feedstocks and the ease of modification. For phosphate remediation, different feedstocks were utilized for BC production including animal wastes [34], solid wastes [42,43], agricultural and plant biomass [44,45]. Moreover, marine microalgae such as *Laminaria japonica* [46], *Undaria pinnatifida* [47], have been investigated

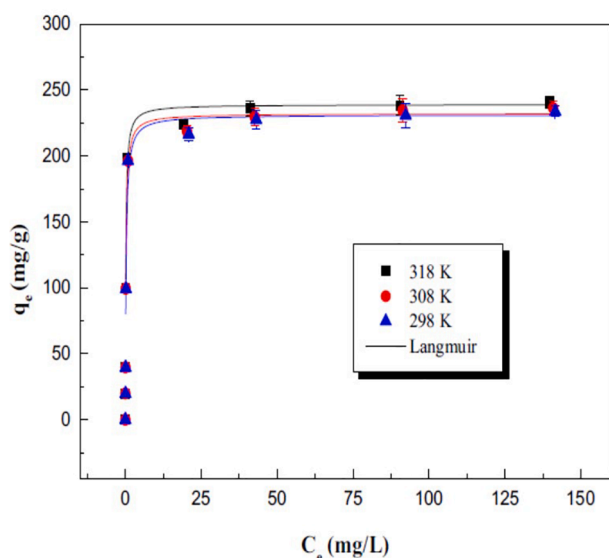


Fig. 1. Adsorption isotherm of phosphate onto 1:1 eggshell and rice straw BC.

for phosphate removal. From an environmental perspective, on the one hand the BC derived from wide range of wastes reduces the environmental burdens, on the other, the exhausted BCs after phosphate removal have been efficiently utilized for soil remediation and as a slow release fertilizer, which is advantageous for BCs amongst other available adsorbents.

The authors have reviewed 110 published manuscripts of the most cited papers on phosphate removal from water using BC. For the readers' convenience, the authors have summarized the reported literature in two sections: unmodified and modified BCs.

2.1. Phosphate removal from water by unmodified BCs

The removal of phosphate by simple prepared BC influenced by different parameters such as the surface area, zeta potential value and the mineral composition of the BC. Most researchers have agreed that the phosphate uptake onto BCs is more dependent on the elemental composition, such as presence of Mg, Ca, Fe or Al elements rather than the surface area. The elemental composition, surface area and porosity of the BCs are highly influenced by the pyrolysis temperature [34,48,49]. Although, the majority of the studies investigated the effect of pyrolysis temperature, there is no agreement on the optimal synthesis temperature for BC production. This is because it is highly dependent on the feedstock used for BC fabrication. For instance, Yao et al. [50,51] studied the phosphate removal by anaerobic digested and undigested sugar beet tailings BC produced at 600 °C. The digested BC demonstrated a higher phosphate removal than the undigested BC, which was attributed to; i) the digested BC has a mesoporous structure with a surface area of 336 m²/g, which is significantly higher than the undigested BC, which had a macro-porous structure with a surface area of 2.6 m²/g, and; ii) the zeta potential of the digested BC is higher than the undigested BC, which increases the affinity of the digested BC to adsorb phosphate ions than the undigested BC. The digested BC illustrates a maximum adsorption capacity of phosphate of 133.1 mg(PO₄³⁻)/g, which is explained by the high Mg nanoparticles content (9.79 wt%).

Magnesium and calcium contents were found to be highly effective for phosphate adsorption onto the BCs [43,48,49]. In this regard, Jung et al. [52] found that peanut shells' BC has the highest Mg and Ca content among soybean stover and bamboo wood BCs. Moreover, the pyrolyzed BC from peanut shells has the highest zeta potential and surface area and accordingly it provides the highest phosphate removal. The BC derived from crab shells, crawfish char and egg shell were found

to have a high Ca content [53–55]. The crab shell BC prepared at 800 °C provides a complete removal of 80 mg/L phosphate using 1 g/L of the BC [53]. For crawfish char BC, the highest Ca content and phosphate adsorption capacity were obtained at the pyrolysis temperature 800 °C. Moreover, the crawfish char BC demonstrated a stable adsorption capacity over the pH range 2–10 [54]. Similar findings were obtained for the BC derived from *Broussonetia papyrifera* leaves, where the adsorption capacity was stable in the pH range 4–11 [56]. Liu et al. [55] studied the effect of the mass ratio of eggshell to rice straw BC. The highest adsorption capacity of 231 mg(P)/g was found for the ratio 1:1 as illustrated in Fig. 1. As can be seen, the adsorption amount slightly increased with temperature and obeyed the Langmuir isotherm model. The chemical precipitation of phosphate ions with the calcium ions was the main mechanism of the adsorption process for the calcium rich BCs [53,55,56].

Marine microalgae has been utilized for the production of BCs and demonstrated a remarkable adsorption capacity of phosphate ions [47,57]. For instance, Jung et al. [47] examined the effect of pyrolysis temperature on BC derived from *Undaria pinnatifida*. Increasing the temperature from 200 to 400 °C was found to increase the surface area and total pore volume, further increasing the temperature decreased the surface properties due to the blockage of the pores as a result of melting, softening and carbonization during the pyrolysis process. The highest phosphate adsorption capacity was 32.58 mg(PO₄³⁻)/g at 30 °C for the BC prepared at 400 °C. This was attributed to the high surface area, point of zero charge (PZC) (8.11) and the existence of Mg and Ca in the BC structure. Jung et al. [57] also utilized *Laminaria japonica* BC for phosphate removal using the powdered BC form and by entrapping the BC into porous structured calcium alginate beads. The powdered and particulate forms demonstrated a maximum adsorption capacity of 160.7 and 157.7 mg(PO₄³⁻)/g at 30 °C, respectively. The high adsorption capacity was attributed to the high content of Mg and Ca onto the synthesized BCs. The study concluded that both forms have heterogeneous surfaces and the adsorption mechanism is an endothermic process.

Amongst the remaining unmodified BCs, sewage sludge and soybean stover BCs demonstrated two of the highest adsorption capacities. For instance, Yin et al. [58] obtained a maximum capacity of 303.49 mg(PO₄³⁻)/g onto the BC synthesized from sewage sludge at 600 °C. The adsorption capacity was attributed to the chemical composition, which is rich in metal oxides and functional groups. The soybean stover had a sorption capacity of 90.9 mg(P)/g as investigated by Karunanithi et al. [59]. The adsorption of phosphate onto the soybean stover BC was attributed to the high surface area and precipitation by the Ca and Mg ions found in the structure of the fabricated BC. The BCs derived from pine [42,60], rice hull [60], maize straw [60], sesame straw [61,62], sugar cane bagasse [63], *Miscanthus giganteus* [63], wood [64], corn cop [64], risk husk [64] and wastewater sludge [65] have demonstrated a phosphate sorption capacity between 15.15 and 116.58 mg(PO₄³⁻)/g. Other BCs have demonstrated poor phosphate adsorption capacity such as elephant grass [34], woody materials [34,49], walnut shell [58], *Thalia dealbata* [66], *Mallee (Eucalyptus polybractea)* [67], horse manure and bedding compost [68] BCs.

Table 2 provides the application of unmodified BCs for the removal of phosphate from aqueous solutions. The majority of the studies with unmodified BCs reported low phosphate adsorption as the adsorbents usually possess a negative surface charge, which is unfavorable for the removal of negatively charged phosphate ions over a wide range of pH [50]. In order to enhance the phosphate adsorption capacity onto the BCs, the introduction of minerals and cationic species is often required.

2.2. Phosphate removal from water by modified BCs

Several chemical elements such as Ca, Mg, Al, Fe, La, Si, Zn, Cu, Ce, Bi and Mn have been used to coat the BC to enhance phosphate removal. BCs can be modified with metal ions by different methods such as:

Table 2

Summary of the reported studies on phosphate removal with unmodified BC from aqueous solutions.

| Adsorbent/ feedstock | Pyrolysis conditions (Temperature and time) | Studied phosphate concentration (mg/L) | N ₂ surface area (m ² /g) | PZC | Elemental composition of | Q _m (mg/g) | Kinetic model | Isotherm | Adsorbent dose D (g/L), Optimum pH _{opt} Equilibrium time (T) | Mechanism of adsorption | Ref |
|--|--|---|--|------|--|---|--|--------------------------------|---|---|------|
| Undigested sugar beet tailings BC | 600 °C, 2 h | 15 – 640 (PO ₄ ³⁻) | 336 | – | Mg: 9.79 wt % Ca: 9.78 wt% Fe: 0.75 wt% Al: 0.24 wt% Zn: 0.03 wt% K: 1.97 wt% | 133.09 (PO ₄ ³⁻) at pH 7, 22 °C | N th order, n = 1.14 | F, L-F | D: 2 pH _{opt} : 5.2 T: 24 h | Electrostatic interactions | [51] |
| Peanut shell BC | 700 °C, 3 h | 1 – 50 (PO ₄ ³⁻) | 328.96 | – | Mg: 0.51 wt % Ca: 7.00 wt% Fe: 0.25 wt% Al: 1.39 wt% K: 0.11 wt% | 7.57 (PO ₄ ³⁻) at pH 7, 30 °C | PSO, Intra particle diffusion | L | D: 2 pH _{opt} : 12 T: 20 h | Chemisorption | [52] |
| Crawfish BC | 800 °C | 2–240 (PO ₄ ³⁻) | – | – | Mg: 0.64 wt % Ca: 41.2 wt% Fe: 909 mg/ kg Al: 932 mg/ kg K: 1.04 wt% | 70.9 (PO ₄ ³⁻) pH 6, 25 °C | PSO | L, F | D: 2 pH _{opt} : 2 – 10 T: 15 min | Ion exchange, precipitation | [54] |
| CaO rich Eggshell and rice straw BC composite | 800 °C, 2 h | 5 – 200 (P) | 25.8 | 5.36 | Si: 2908 mg/ kg Ca: 34.6 wt% | 231 (P) at pH 7, 25 °C | PSO | L | D: 0.25 pH _{opt} : 5 – 11 T: 6 h | Precipitation | [55] |
| Broussonetia papyrifera leaves BC | 500 °C, 2 h | – | 9.53 | – | Mn: 0.14% | 35.63 at pH 7, 25 °C | PSO, Intra particle diffusion | L at 30 °C F at 25 °C | D: 5 pH _{opt} : 4 – 11 T: 120 min | Surface precipitation | [56] |
| Undaria pinnatifida roots BC | 400 °C, 2 h | 1 – 200 (PO ₄ ³⁻) | 70.29 | 8.11 | Mg: 1.35 wt % Ca: 1.73 wt% K: 0.69 wt% | 32.58 (PO ₄ ³⁻) at pH 7, 30 °C | – | L | D: 1 pH _{opt} : - T: | Endothermic adsorption. | [47] |
| Laminaria japonica powder BC | 600 °C, 1 h | 5 – 1000 (PO ₄ ³⁻) | 79.95 | – | Mg: 2.61 wt % Ca: 6.15 wt% K: 28.29 wt% | 160.7 (PO ₄ ³⁻) at pH 6, 30 °C | PSO | L-F | D: 1 pH _{opt} : T: 24 h | – | [57] |
| Ca-alginate granular beads Laminaria japonica BC | 600 °C, 1 h | – | 242.34 | 8.42 | – | 157.68 (PO ₄ ³⁻) at pH 6, 30 °C | – | – | D: 1 pH _{opt} : 6 T: 24 h | – | |
| Sewage sludge BC | 600 °C, 3 h | – | 31.35 | 11.2 | Mg: 1.99 wt % Ca: 19.38 wt % Fe: 3.16 wt% Al: 6.49 wt% Si: 8.33 wt% K: 0.82 wt% | 303.49 (PO ₄ ³⁻) at 25C | PSO | L-F | D: 2 pH _{opt} : 4 T: 5 h | Electrostatic interactions, ligand exchange | [58] |
| Soybean stover BC | 700 °C, 3 h | 10 – 200 (P) | 420.33 | – | – | 90.9 (P) at pH 5.5, 40 °C | PSO | L, F | D: 4 pH _{opt} : 5.5 T: 24 h | Surface precipitation | [59] |
| Pine sawdust BC | 750 °C, 15 min | 10 – 60 (PO ₄ ³⁻) | 219 | – | – | 15.11 (PO ₄ ³⁻) at 25 °C | PSO | F | D: 1 pH _{opt} : - T: 120 min | – | [42] |
| Maize straw BC | 350 – 550 °C | 100 – 2000 (P) | 4.05 | – | – | 9.47 (P) at RT | – | L | D: 100 pH _{opt} : - T: 24 h | – | [60] |
| Rice hull BC | | | 8.2 | | | 12.52 (P) at RT | | | | | |
| Pine BC | | | 97.2 | | | 14.48 (P) at RT | | | | | |

(continued on next page)

Table 2 (continued)

| Adsorbent/ feedstock | Pyrolysis conditions (Temperature and time) | Studied phosphate concentration (mg/L) | N ₂ surface area (m ² /g) | PZC | Elemental composition of | Q _m (mg/g) | Kinetic model | Isotherm | Adsorbent dose D (g/L), Optimum pH _{opt} Equilibrium time (T) | Mechanism of adsorption | Ref |
|--|--|---|--|------|--|--|------------------|-----------------|---|---|------|
| Sesame straw BC | 600 °C, 2 h | 0 – 400 (P) | 319.4 | – | Mg: 4861 mg/kg Ca: 0.54 wt% Fe: 14.98 mg/kg K: 9.4 mg/kg Mg: 0.75 wt % Ca: 3.7 wt% Al: 0.05 wt% | 15.46 (P) at 25 °C | – | F | D: 2 pH _{opt} : - T: - | Electrostatic interactions and metal-ion complex formation. | [61] |
| Sesame straw BC | 700 °C | 5 – 500 (P) | 413 | – | – | 116.58 (PO ₄ ³⁻) at 25 °C | PSO | L-F | D: 2 pH _{opt} : - T: 12 h | – | [62] |
| Sugar cane bagasse BC | 700 °C, 60 min | 25 – 400 (P) | 131 | – | – | 13.21 (P) at pH 7, 20 °C | – | L | D: 2 pH _{opt} : 3 – 4 T: - | Ion exchange | [63] |
| Miscanthus giganteus BC | | | 244 | | | 16.1 (P) at pH 7, 20 °C | | | | | |
| Wood BC | 600 °C, 10 h | 25 – 150 ppm (P) | 147 | – | – | 11.98 (P) at pH 7, 25 °C | PSO | L, F, Timken | D: 1.25 pH _{opt} : - T: 10 h | Electrostatic interactions, ligand exchange | [64] |
| Corncoobs BC | | | 123 | | | 11.4 (P) at pH 7, 25 °C | | | | | |
| Rice husks BC | | | 11 | | | 8.09 (P) at pH 7, 25 °C | | | | | |
| Sawdust BC | | | 7 | | | 10.07 (P) at pH 7, 25 °C | | | | | |
| Sewage sludge BC | 650C, 30 min | 5 – 80 (PO ₄ ³⁻) | 149.47 | 3.27 | Ca: 0.52 atomic% Fe: 3.35 atomic% | 15.15 (PO ₄ ³⁻) at 25 °C | – | L | D: 4 pH _{opt} : 7 T: - | Ligand exchange, columbic interaction, Lewis acid base interaction, surface precipitation | [65] |
| CO2 activated Thalia dealbata BC | 700 °C, 2 h | – | 223.1, N ₂ 228.3, CO ₂ | – | Mg: 4.42 g/ kg Ca: 19.66 g/ kg Fe: 0.64 g/kg Al: 0.44 g/kg | 4.96 (P) pH 7, RT | – | L | D: 4 pH _{opt} : - T: - | Surface precipitation | [66] |
| Eucalyptus polybractea BC | 720 °C, 20 min | 10 – 528 (P) | 233 | – | Mg: 0.2 atomic% Ca: 1.3 atomic% K: 0.3 atomic % | 3.66 (P) at RT | Elovich | F | D: 3.33 pH _{opt} : - T: 1 | – | [67] |

1. Impregnation method (pre and after pyrolysis);
2. Electrochemical modification;
3. Enriching of biomass with metals by using the spiking solutions (bioaccumulation);
4. Co-pyrolysis of the biomass and natural sources of metals ions.

The most well-known method of BC modification is impregnation. The impregnation can be performed prior to pyrolysis by mixing the feedstock (biomass) of the BC with a concentrated metal substrate, followed by pyrolysis at a specified temperature, or it can be conducted subsequent to pyrolysis in which the pyrolyzed BC is then treated with concentrated metal solution. The impregnation method is material and time consuming. As such, Jung et al. [69] provided a novel approach of BC modification by electrochemically modifying the biomass for 10 min followed by thermal pyrolysis. This method was modified by the same group to obtain the Al/Mg modified BC by using an aluminum electrode

and concentrated Mg containing solution as an electrolyte [70]. Another method for enriching the feedstock with Ca and Mg ions was by the irrigation of tomato leaves with metal spiked solutions [71]. Mosa et al. also used this method to obtain water hyacinth (*Eichhornia crassipes*) plants BC by irrigating the feed stock with spiked Fe, Cu, Zn, Mn solutions [72]. After pyrolysis, the obtained BC showed an increase in the spiked metals content compared to un-spiked irrigated plants. Finally, mixing the BC feedstock with natural materials rich with Ca and Mg such as montmorillonite [73], dolomite [74], phosphogypsum [75] and bentonite [76,77] ions followed by pyrolysis is another method for preparation of the modified BCs.

BC modification with metals has the ability to alter the surface properties of BCs such as the surface area, surface charge, pore diameter and surface functional groups. The surface area of the engineered BCs was found to change according to the type of ions used for the modification. Although most studies have reported a decrease in the surface

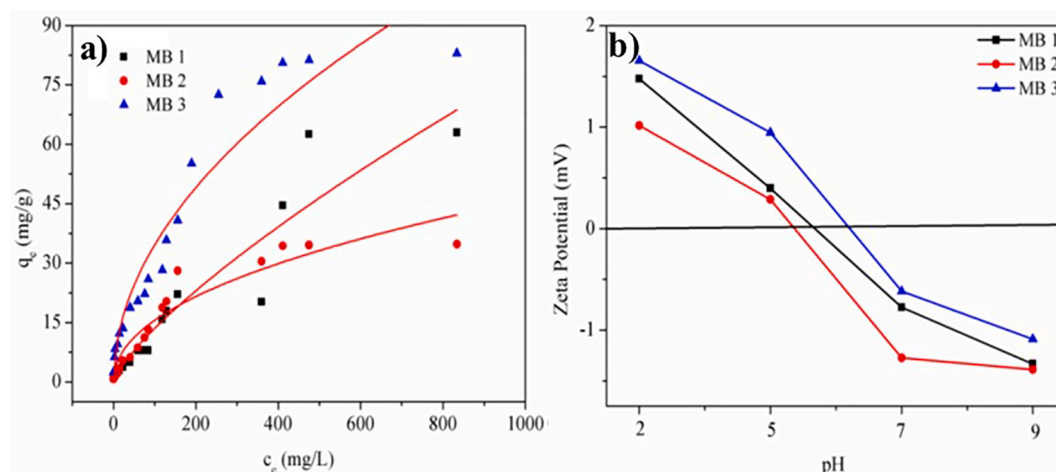


Fig. 2. a) Adsorption isotherm, and b) Zeta potential measurements of phosphate removal by iron modified BC by different methods [93].

area and porosity of BCs with modification due to pore blockage with metal ions, for example as for magnetic BCs [78–80], several studies have reported an enhancement in the porosity and surface area of BCs, which have resulted in offering more adsorption sites for Ca- [57], Mg- [81], La- [82,83], Al- [84] and LDH [85] modified BCs. Whether the surface area was decreasing or increasing, the adsorption capacity of phosphate was found to be significantly enhanced with modification. It was observed that all of the metal ions used for modification have shifted the PZC to a higher pH value and/or decreased the surface charge negativity of the adsorbent. This consequently has resulted in an increase in the adsorption capacity of phosphate.

2.2.1. Magnetic modified BCs

Magnetic BCs have been widely used for phosphate remediation because of the possibility of applying the magnetic field for adsorbent recovery after the adsorption process [86,87]. Although iron oxide doping onto the BCs decreases the porosity and surface area of the raw BC due to the blockage of the pores, the iron oxide doped BCs have been found to enhance the adsorption capacity of phosphate [88,89]. Iron is doped onto BC by different methods such as impregnation [90,91], chemical co/wet-precipitation [41,80] and pre-activation followed by iron treatment [92]. In this regard, Yang et al. [93] used three modification methods of iron oxide onto activated sludge BC. Iron oxide co-precipitation under nitrogen (MB 1), under an air atmosphere (MB 2), and impregnation (MB 3) methods. The results illustrated that the impregnated BC has the highest adsorption capacity as illustrated in Fig. 2a. The maximum phosphate adsorption capacity onto the impregnated BC was 111 mg(PO_4^{3-})/g at pH 7 and 22 °C. The authors concluded that the phosphate removal efficiency of Fe^{3+} attached BC was better than Fe_3O_4 because it has a higher isoelectric point, which is evident from Fig. 2b. A couple of studies have reported phosphate removal by granulated iron modified BCs [94,95]. The authors determined that the adsorption capacity increased with granulation, which was attributed to the higher mesopore and micropore surface areas of the granulated BCs. In addition, it has a higher weight content of iron and oxygen elements.

Iron oxide has different forms, namely, magnetite, ferrihydrite, goethite and hematite. Zhang et al. [96], found that the maximum adsorption capacity was 22.14, 18.49, 13.81 and 9.408 mg(PO_4^{3-})/g at pH 2 for goethite, ferrihydrite, hematite, and magnetite BC, respectively. The order was consistent with the PZC of the modified BCs, in which goethite has the highest PZC and the magnetite has the least PZC. The adsorption rate of phosphate onto iron oxide/magnetic BCs generally followed the pseudo 2nd order kinetic model indicating a chemisorption process. The phosphate uptake by iron oxide doped BCs was mainly dominated by electrostatic attraction, ligand exchange and ion exchange

mechanisms [78,97–100]. An exception is found for the case of ferric oxide hydrate doped onto the digested swine manure BC, whereby the chemisorption mechanism was dominated by the hydrogen bond interaction [101]. This composite demonstrated the highest adsorption capacity of iron decorated BCs of about 53.83 mg(P)/g.

2.2.2. Calcium/magnesium modified BCs

Calcium and magnesium ions were of significant interest for phosphate capture [102]; the Ca and Mg contents in the unmodified BCs were the main reason for the high removal rate of phosphate [50,51]. Moreover, these elements are nontoxic, inexpensive and widely available. BC modification with Mg and Ca can be conducted by impregnation [44,103–105], bioaccumulation [71], electrochemical deposition [69,106] and co-pyrolysis of the BC feedstock with the natural source of Mg/Ca ions [73,74]. Surface characterization of Mg-modified BCs indicated that the Mg is fixed on the surface of the BCs as MgO or Mg (OH)₂. The existence of Mg nanoparticles shifts the PZC to high alkaline values and the PZC of the Mg modified BC is approximately 12 [70,107]. This facilitates the electrostatic interactions between the negatively charged phosphate ions and Mg-BCs leading to reported phosphate adsorption capacities reaching 620 mg(P)/g for Mg electrochemically modified BC [69]. Furthermore, Mg doping onto the BCs were found to increase the surface area and enhance the porosity of the BCs, which in turn improved the adsorption capacity of phosphate [81,108,109]. Phosphate was found to be adsorbed onto the Mg modified BCs by chemical precipitation, struvite crystallization ($\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$) and ligand exchange mechanisms [81,110–112]. Calcium nanoparticles found on the BC as CaO or Ca(OH)₂ structures [113]. The phosphate ions were adsorbed by Ca modified BCs by chemical precipitation, ligand exchange, and electrostatic interactions [103,113,114]. The XRD and FTIR analysis also found that crystallization of phosphate ions with Ca (OH)₂ significantly promoted the adsorption process reaching an adsorption capacity of 314.2 mg(P)/g at 25 °C [115]. The adsorption kinetics of phosphate onto Ca and Mg modified BCs are mostly described by the pseudo 2nd order model. The Mg modified BC demonstrated faster kinetics in which the equilibrium was reached in 5 – 35 min in several studies [44,116,117].

The Mg modified BCs were doped by iron to enhance the adsorbent recovery after the adsorption process [107]. Even with a surface area reduction, the adsorbents demonstrated high capabilities toward phosphate removal [118,119]. Granulation of alginate/Ca or Mg modified BC have also resulted in a decrease of the surface area. However, the adsorbent illustrated remarkable adsorption capacity of 394.35 (PO_4^{3-}) [106]. Adsorbent granulation has provided an advantage to be used in column studies [106,120].

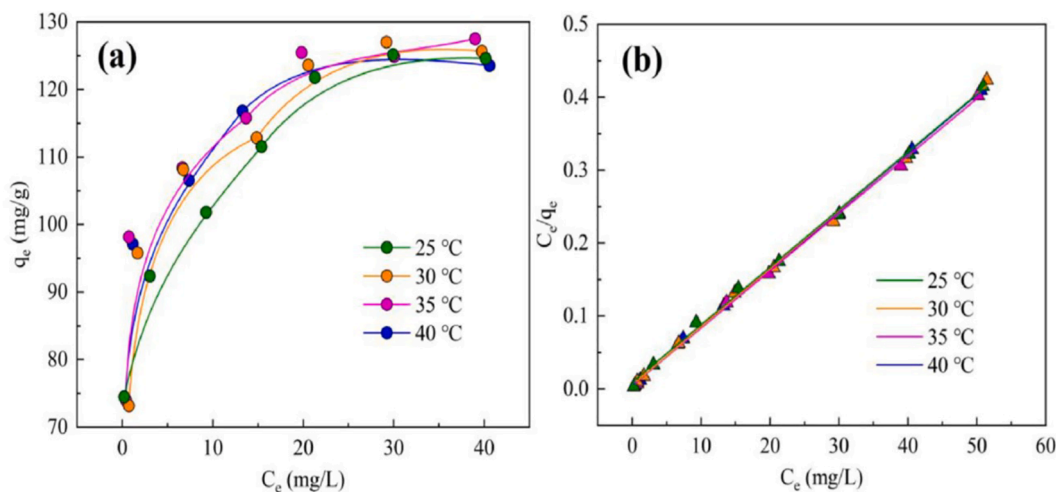


Fig. 3. a) Effect of temperature on the adsorption capacity of phosphate onto La-modified platanus ball fiber BC, b) fitting lines of Langmuir model [82].

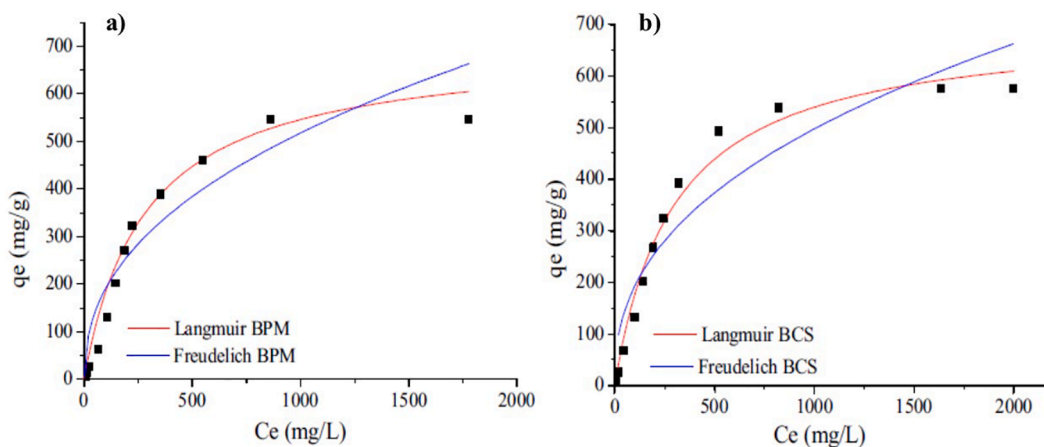


Fig. 4. Adsorption isotherms of phosphate removal by a) Al-modified poultry manure BC and b) Al-modified sugar cane straw BC.

2.2.3. Lanthanum modified BCs

Lanthanum (La) is of increasingly popularity due to its selectivity and strong affinity towards phosphate ions. La is doped on the BC as a singly element or incorporated with other materials such as iron [83,121,122], chitosan [123] or magnesium [124] both in powder and granulated forms [124]. The La modification can be conducted by the chemical co-precipitation method as described in several studies [83,125,126]. Similar to Ca and Mg decoration, La is formed on the BC surface as an oxide or hydroxide [45,126]. The addition of La is found to significantly decrease the negativity of the BC, and shifts its PZC to alkaline medium leading to improved removal of phosphate ions [127]. The adsorption of phosphate onto La modified BCs is mostly described by Langmuir isotherm and pseudo 2nd order kinetic model indicating a chemisorption process. Phosphate is adsorbed by the La modified BCs as a result of the electrostatic interactions, precipitation, ligand exchange and complexation interactions [82,121,122,124–126]. The maximum achieved adsorption capacity of phosphate onto La modified BC was 148.11 mg(P)/g at 35 °C and pH 6 for La-modified platanus ball fiber BC [82], this adsorption capacity was not affected by temperature and best fitted with the Langmuir model as seen in Fig. 3a and Fig. 3b.

2.2.4. Aluminum modified BCs

Aluminum has also been used for BC modification in phosphate removal. BCs were doped by Al nanoparticles by immersing the feed-stock in Al containing solutions [128,129], or by the novel

electrochemical modification method using Al electrodes [46,130,131]. In both methods, Al was demonstrated to be doped as AlOOH on BC. Moreover, several studies have reported an enhancement in the surface area with Al doping, which offers more adsorption sites [128,130,132]. Poultry manure and sugarcane straw BC modified with Al showed the highest ever reported phosphate adsorption capacity onto BCs of 701.65 and 758.96 mg(P)/g, respectively [129]. Isotherm analysis of both of the modified BCs followed the Langmuir isotherm model as illustrated in Fig. 4. The authors attributed the high phosphate sorption capacity to the high affinity of Al toward phosphate ions. The adsorption kinetics of phosphate onto Al modified BCs following the pseudo 2nd order kinetic model indication a chemisorption process. The adsorption mechanisms include electrostatic interactions and precipitation [132]. The simultaneous modification of Al with other elements such as Mg [70,84,131], Fe [133], and Mn [134] have been investigated. Amongst these combinations, the Mg/Al modified BC showed the highest adsorption capacity of 887 mg(PO_4^{3-})/g by using Mg/Al electrochemically modified BC. Yin et al. [70] recommended the bicomponent Mg/Al modified BC for the treatment of eutrophic water, the existence of Mg offers new adsorption sites leading to higher adsorption capacity. Similarly, Zheng et al. [84] found that the Mg/Al modified BC has the highest phosphate adsorption capacity compared to single modified BC. This was attributed to the higher content of AlOOH on the BC surface and abundant functional groups. In addition, both chemical and physical adsorption occurs on the Mg/Al modified BC.

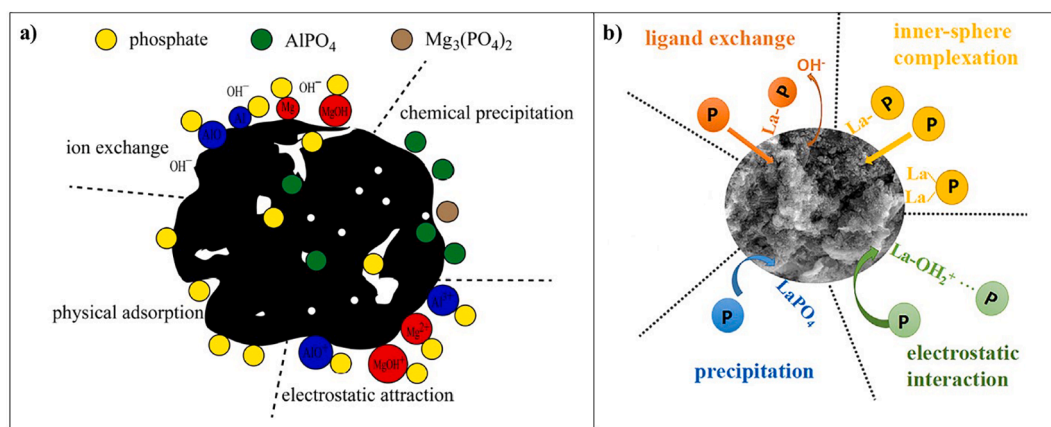


Fig. 5. Adsorption mechanisms of phosphate onto a) Mg/Al modified BC and b) La modified magnetic BC [84,121].

2.2.5. Layered double hydroxides modified BCs

Layered double hydroxides (LDH) have been also used for BC doping. This increased the PZC and the surface area of the raw BC leading to a better adsorption capacity of phosphate [135]. In general, the LDHs were doped onto BCs by chemical co-precipitation/functionalization [135–138]. One study reported the electro-assist modification of Mg/Al LDH BC [79]. Different combinations of doping elements were investigated for phosphate removal, the Mg/Al combination is the most common LDH for phosphate removal because of the affinity of phosphate ions toward Mg and Al ions. In this regard, Wan et al. [137], found that BC doped with Mg/Al LDH has a higher phosphate removal capability than that doped with Mg/Fe LDH. It was indicated that Mg/Al LDH has higher affinity to adsorb phosphate ions. In addition it has a higher stability in the aqueous solutions than the Mg/Fe LDH. Lower stability of Mg/Fe LDH hinder the full exposition of the active sites for phosphate, and hence, lower phosphate removal.

In the same manner, Yang et al. [85] concluded that the Mg/Al combination onto BC has higher phosphate adsorption capacity compared to Ni/Fe and Zn/Al LDHs, which is also attributed to the high affinity of phosphate toward Al and Mg ions. The ratio of Mg to Al onto BC was investigated by Li et al. [136] who found that the ratio of 4:1 of Mg to Al has the highest surface area and maximum phosphate adsorption capacity. This was also attributed to the higher interlayer space for the ratio 4:1, which enhances the accessibility of the active sites. Moreover, Lee et al. [139] also found that BC with Mg to Al ratio of 2:1 has a higher phosphate removal than at 1:1 ratio. The phosphate adsorption onto Mg/Al LDHs modified BCs was controlled by electrostatic interactions, precipitation, ion exchange, memory effect and inner and outer sphere complexes [135,137–140]. The Mg/Al LDH modified BC demonstrated fast kinetics, in which the equilibrium was reached in 1 h [135,137], and the maximum reported phosphate adsorption capacity was 172 mg(P)/g at room temperature [137].

2.2.6. Other modified BCs

BC modification with cerium, bismuth and silicon oxide are less investigated compared to the aforementioned elements. BC functionalized with cerium oxide was reported by Feng et al. [141], who determined the maximum phosphate capacity of 77.52 mg(PO_4^{3-})/g, and where the equilibrium was reached after 1–1.5 h. Cerium modified BC was found to have lower capacity than the La modified BC as presented by Wang et al. [83]. This was attributed to the higher PZC of La modified BC. The BC modified by bismuth demonstrated higher adsorption capacity of approximately 125.4 mg(P)/g and its equilibrium was achieved in 2 h [142]. The BC decorated with SiO_2 demonstrated a significant increase in the surface area with a maximum phosphate adsorption capacity 159.4 mg(PO_4^{3-})/g, while equilibrium was reached in 5–10 h. The ion exchange, chelation process and electrostatic interactions

mechanisms were used to explain the adsorption process of phosphate onto SiO_2 modified BC.

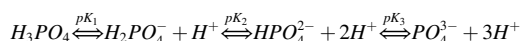
A few studies have reported a comparison between the doped elements on the BC. Saadat et al. [143], found that Ca modified BC has the highest phosphate removal followed by $\text{Mg} > \text{Al} > \text{Fe} > \text{Cu}$. Mosa et al. [72] compared the phosphate removal by Fe, Cu, Zn and Mn modified BC. Modification was conducted by the bio-accumulation process, where the feedstock was irrigated with concentrated metal solutions and then pyrolysed after growing. The Fe-BC demonstrates the highest phosphate adsorption capacity of 31.55 mg(PO_4^{3-})/g followed by $\text{Zn-BC} > \text{Cu-BC} > \text{Mn-BC}$. The higher adsorption capacity of Fe-BC is related to his lowest electronegativity and the highest surface area. The adsorption process was mainly controlled by chemical precipitation with a slight contribution of other mechanisms such as electrostatic interactions and complexations. However, it is difficult to claim that one of the elements is better amongst the others for all kinds of BCs. The type of the feedstock, pyrolysis method and pyrolysis conditions highly influence the properties of the BC and their reactivity with metals.

Functionalization of corncobs BC with carboxylic and amino groups was investigated by Faheem et al. [144]. The phosphate uptake by functionalized BC was controlled by electrostatic interactions. The adsorption process followed the pseudo 1st order kinetic model and the isotherm data were in compliance with the Langmuir model, indicating a physisorption process and monolayer coverage of phosphate ions. The maximum capacity and equilibrium time were 57.47 mg(P)/g and 75 min. Table S1 illustrates the outcomes of the literature of phosphate removal by modified BCs.

3. Adsorption mechanisms

The physical and chemical interactions between phosphate and BC governs the removal of phosphate from aqueous solutions. Understanding the adsorption mechanism is of significant importance as it is interconnected to the adsorption isotherms, kinetics, capacity and adsorption thermodynamics. For the reader's convenience, the mechanisms of the phosphate adsorption with BCs that have been reported in the literature are summarized in Table's 2 and S1. These mechanisms might vary and include electrostatic interactions, Lewis acid–base interaction, ion exchange, ligand exchange, precipitation, crystallization, inner sphere complexation, outer sphere complexation and hydrogen bonding (Fig. 5).

Most studies suggest the adsorption of phosphate onto BCs is governed by electrostatic interactions. BC as a carbon based adsorbent possesses a negative surface charge in aqueous solutions and phosphate ions dissociate with pH as follows [12];



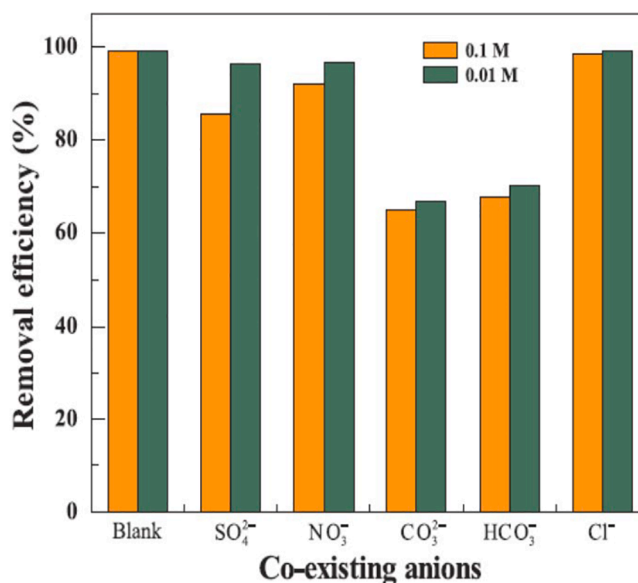


Fig. 6. Effect of coexisting anions on phosphate removal by La modified magnetic BC [122].

where; pK_1 , pK_2 , pK_3 values are 2.13, 7.20 and 12.33, respectively.

The electrostatic interaction is highly affected by the pH of the solution and the PZC of the adsorbent. Thus, attractive electrostatic interactions occur when the solution pH is lower than the PZC value of the adsorbent. Subsequently, the negatively charged phosphate ions are electrostatically adsorbed by positively charged adsorbent particles. When the solution pH is higher than the PZC of the adsorbent, the electrostatic repulsion between the phosphate ions and negatively charged BC surface occurs. However, several studies have reported notable values of phosphate removal at feed pH values above the PZC value of BC [84,122,126], implying that apart from electrostatic interactions, other mechanisms, for example ion exchange are involved in the phosphate adsorption process [63,136]. It should be noted that the electrostatic mechanism occurs in both chemical and physical adsorption processes. Compared to other mechanisms, electrostatic interactions are considered easy and reversible adsorption steps [26].

Ion exchange is related to the ion replacement in which a phosphate ion replaces an ion from the structure of the BC. Often ion exchange is related to the outer sphere complexation. This kind of adsorption is considered to be reversible where the phosphate ions can be recovered from the BC surface. Iron oxide modified BCs are an example of phosphate removal by an ion exchange mechanism [93–95].

The adsorption mechanism via ligand exchange is also related to ion replacement, for instance, the phosphate groups replace the hydroxide groups within the BCs [85]. This mechanism is widely used to explain phosphate adsorption onto LDH modified BCs [79,85,140]. Phosphate adsorption by means of ligand exchange is related to the formation of inner sphere complexes, and this complexation results in stronger binding of phosphate ions with BC compared to ion exchange [26].

Precipitation of low soluble phosphate salts occurs when the concentration of the phosphate exceeds its solubility. It can also occur at lower concentrations when the finite volume beside the adsorbent mineral surface is oversaturated with phosphate according to the principle of thermodynamic solubility [37]. Precipitation of the phosphate species on the adsorbent surface has been widely cited in the literature for Ca, Mg, Al, Fe and La modified BCs [72,74,103,125]. For instance, Wang et al. [125] found that the precipitation of LaPO_4 is one of the dominant mechanisms of phosphate adsorption onto La modified BC. Liu et al. determined that the precipitation of phosphate as hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ was the controlling mechanism of phosphate removal by Ca rich BC. Phosphate precipitation can be detected by XRD, XPS, FTIR

and SEM analysis as detected for Ca, La and Mg modified BCs [103,120,125,145]. Usually this process is fast and precipitated phosphates are not easily recovered. Apart from the precipitation mechanism is the formation of phosphate crystals onto Ca and Mg modified BCs [74,76,110,115]. Usually, crystallization of phosphate occurs as struvite for Mg and Ca modified BCs. More information related to struvite crystallization of phosphate is available [147].

Lewis acid-base interactions were found to be a controlling mechanism for phosphate removal with sewage sludge BC [65] and La modified BC [123]. The excess of hydrogen ions at acidic conditions can protonate the active adsorption sites and the BC behaves as a weak acid, which acts as an electron acceptor. Alternatively, a phosphate ion acts as a weak base and electron donor. At alkaline conditions, the excess of hydroxide groups deprotonate the active adsorption sites on BC surface, which act as a weak base, while phosphate ions behave as a weak acid. This allows for the Lewis acid base interaction between phosphate anions, and the active adsorption sites, such as the case of La modified BC [123] and the Fe found in the structure of the sewage sludge BC [65].

Hydrogen bonding is another mechanism suggested for the adsorption of phosphate species onto BC modified with ferric oxide [101]. Hydrogen bonding is a result of the interaction between hydrogen atoms in H_2PO_4^- and HPO_4^{2-} ions and oxygen containing groups of the ferric oxide.

4. Adsorption thermodynamics

Studying the thermodynamic parameters, i.e. enthalpy ΔH° , Gibbs free energy ΔG° and entropy ΔS° of adsorption, can provide essential information related to the spontaneity, heat of adsorption and randomness of the adsorbate ions at the solid/liquid interface. The negative values of ΔG° indicate that the adsorption process is spontaneous. Negative values of ΔH° indicate that the adsorption process is exothermic and the adsorption amount decreases with temperature, while positive values of ΔH° point to endothermic adsorption and the adsorption amount increases with temperature. The ΔS° parameter represents the randomness of the adsorption process: positive values of ΔS° indicate an increase in randomness, which is favorable for chemical reactions.

The ΔG° values were found to be negative for all studies that investigated the adsorption thermodynamics of phosphate onto BCs indicating that this adsorption is spontaneous in nature. Similarly, ΔS°

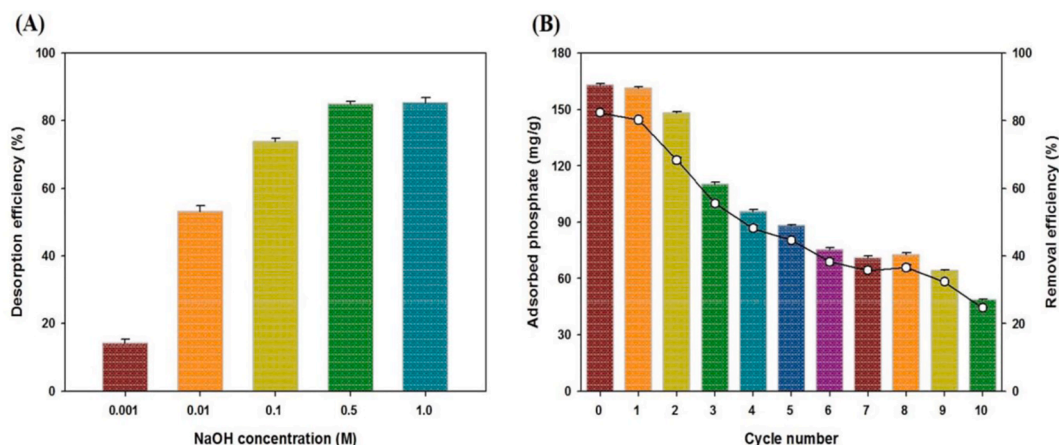


Fig. 7. a) Effect of NaOH concentration on the phosphate desorption efficiency, and b) Phosphate sorption capacity and desorption efficiency with cyclic number using 0.5 M NaOH, from magnesium ferrite magnetic BC [119].

values were also found to be positive representing an increase in randomness at the liquid/adsorbent interface and the high affinity of phosphate ions toward the adsorbent surfaces. However, ΔH° values were found to be negative for most of the cases indicating an endothermic adsorption process [42,44,55,58,59,75,78,80,102,106,113,119,122,125,139,140,142,148]. Several exceptions include phosphate removal onto cotton stalk BC [43], wood, corncobs, rice husks, sawdust BCs [64], iron modified BCs [99,101] where the adsorption process was found to be exothermic.

5. Effect of competitive ions

The coexistence of different ions in the feed solution affect the equilibrium adsorption capacity of phosphate with BCs. In general, wastewater, municipal and industrial water streams consist of different ions that compete with each other on the adsorption sites. As such, the effect of different anions including NO_3^- , Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- and F^- and cations such as Ca^{2+} and Cd^{2+} on the phosphate adsorptive removal by BCs were reviewed [76,144]. Moreover, the effect of the organic matter “humic acid” on the adsorption capacity of phosphate has been extensively investigated in the literature [89,126].

Regarding different anions, it can be concluded that the divalent anions with higher charge density such as SO_4^{2-} , CO_3^{2-} possess a higher impact on the adsorption capacity of phosphate than monovalent anions such as Cl^- and NO_3^- . The presence of CO_3^{2-} ions was found to significantly reduce the adsorption capacity of phosphate in several studies [86,93,146]. For example, 31.6% reduction in phosphate removal by La modified magnetic BC was reported in the presence of 0.1 mol/L of CO_3^{2-} (Fig. 6). This effect can be explained by a different phenomenon. Firstly, the addition of CO_3^{2-} increases the pH of the solution which is unfavorable for phosphate removal [139], secondly, CO_3^{2-} ions exert high affinity towards the active adsorption sites and finally, for the cases of La modified BCs, the formation of $\text{La}_2(\text{CO}_3)_3$ is easier than LaPO_4 due to the lower solubility of lanthanum carbonate [82,122]. Moreover, Jing et al. [76] found a significant decrease in the adsorption capacity of phosphate onto Mg modified BC when it coexists with CO_3^{2-} ions which was attributed to the competition for Mg^{2+} ions to form amorphous magnesium carbonate. Similar observations were reported for the reduction in phosphate removal in the presence of HCO_3^- ions [51]. The effect of SO_4^{2-} ions on phosphate adsorption was attributed to the competition for the adsorption sites. The ionic radius of SO_4^{2-} is very close to the ionic radius of phosphate, which makes them compete for the same adsorption sites [110,136]. The presence of F^- ions was found to have a significant negative effect on the removal of phosphate, which was attributed to; i) F^- ion which has the highest electronegativity and can

easily combine with the protonated adsorbent surface [136], ii) F^- ion can form inner sphere complexes with La modified BC and consequently decreases the adsorption capacity of phosphate [126], and iii) the competition on the vacant adsorption sites [79]. It should be noted that the effect of the coexisting anions varies according to the BC structure and composition. Some adsorbents demonstrated high selectivity toward phosphate ions and were less affected by the addition of coexisting anions such as La modified magnetic pineapple BC [121], MgO modified peanut shell BC [117] and Mg/Al LDH modified date-palm BC [140].

The presence of humic acid (HA) was found to decrease the adsorption capacity of phosphate onto the different BCs. This effect was more significant with increasing initial HA concentration [82]. HA exerts an affinity toward the active adsorption sites and hence competes with phosphate. Moreover, HA molecules are rather polydisperse with a radius of 1.2–4 nm and can block the pores and prevent the phosphate ions from diffusing into the internal pores of the adsorbent [126]. Zhong et al. [89] explained the reduction of phosphate removal onto Fe modified BC in the presence of HA by the fact that HA can be adsorbed by ligand exchange mechanism with hydroxide ions and this will reduce the adsorption capacity available for phosphate.

On the other hand, the presence of Ca^{2+} ions in the feed has a positive impact on phosphate removal due to formation of low soluble calcium phosphate [76,105,110]. Tang et al. [126] concluded that the coexisting Ca^{2+} ions react with phosphate to form ion pairs CaHPO_4 , which can be easily adsorbed. For La modified BC, Ca^{2+} also form tertiary complexes with the adsorbed phosphate. Similarly, Cd^{2+} ions have promoted the adsorption process of phosphate onto COOH/amino functionalized BC because the interaction between Cd^{2+} and carboxylic ions can offer new adsorption sites for phosphate [144]. Additionally, the coexistence of ammonia has promoted the adsorption of phosphate from urine solutions on Mg modified BC [116]. For Mg modified BC, the coexisting ammonium has also improved the adsorption of phosphate due to the formation of struvite phosphate mineral of $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ formula [58,105].

Studying the effect of coexisting ions on phosphate removal is of significant importance when dealing with multi-component aqueous solutions, real surface water and wastewaters. Despite some conclusions that can be deduced from the available literature, there is a lack of research in this field and the effect of coexisting anions, cations and the presence of organic compounds on removal of phosphate with BCs requires further investigation.

6. Desorption studies and reuse of exhausted BCs

6.1. Phosphate desorption

Desorption of phosphate from BCs has been studied by using different regeneration solutions based on acids, bases and salts. The selection of a desorption solution depends on the desorption efficiency, the number of regeneration cycles, and the effect of the solution on the doped elements in case of the modified BCs.

Salts were found to achieve a good desorption efficiency wherever a physical adsorption or a weak chemical bonding between phosphate and the adsorbent surface was occurring. For instance, Sarkhot et al. [49] obtained a 60% of desorption efficiency from mixed BC using CaCl_2 salt for elution. Novais et al. [129] obtained more than a 92% of phosphate desorption from Al-doped BCs using NaHCO_3 as a desorption solution. In contrast, NaHCO_3 was found to be ineffective for phosphate desorption from Mg modified BC [118]. Moreover, salts such as NaCl [118], KCl [48,93] were inefficient for phosphate desorption, where a strong chemical bonding occurred between phosphate and the adsorbent surfaces. In these cases, acid and bases were employed for phosphate desorption and regeneration experiments.

Acids and NaOH alkaline solutions were found to be more efficient for phosphate desorption compared to salt solutions. The use of highly acidic or basic mediums can shift the pH to be lower than 2 or higher than 12, these pH ranges are considered unfavorable for phosphate adsorption. At pH values lower than 2, the phosphate exist as uncharged H_3PO_4 , which hinder the effect of electrostatic interactions, and when the pH is higher than 12, the phosphate ions are negatively charged and will be repelled from the negatively charged adsorbent surface. Moreover, the competition between phosphate and hydroxide ions on the adsorption sites at high pH will also decrease the phosphate removal. Different acid solutions were used for phosphate desorption from BCs such as HCl [118], H_2SO_4 [64,78,129] and citric acid [63]. The desorption efficiency of citric acid solutions was 47% after the first adsorption cycle [63], and it was 37.5% for HCl solution [118]. The desorption efficiency was higher for sulfuric acid reaching 80% in some cases [64,78,129]. The alkaline NaOH solutions were found to be the most commonly used solution for phosphate desorption from BCs [79,82,89,93,96,107,108,119,121–123,133,134,138–140,146]. Moreover, the NaOH solutions were found to be more efficient than acidic solutions reaching more than 70% of desorption efficiency after 5 adsorption/desorption cycles [107,108,122,133,134,139,146]. Li et al. [136] found that higher desorption efficiencies were achieved at pH 10.9 than at pH 1.05. Notably, most studies demonstrated a lower adsorption capacity of phosphate in basic media than in acidic media, which might be the reason behind the higher desorption efficiency of phosphate using NaOH solutions. Although, NaOH solutions were found effective for the desorption of phosphate from BCs in the first adsorption/desorption cycle, the adsorption efficiency was found to decrease with increasing regeneration cycles. The adsorption efficiency was found to decrease reaching more than 60% in the first 3–5 adsorption/desorption cycles [89,121,138,139], while it reduced significantly for the studies that have conducted more than 5 adsorption cycles [119]. This was mainly attributed to the leakage of the doped elements such as SiO_2 , Fe, and La with elution [89,93,96,121,146].

Desorption efficiency also depends on the concentration of the NaOH solution. For instance, Jung et al. [119], illustrated that increasing the NaOH concentration from 0.001 to 0.5 mol/L increased the desorption efficiency from 14.2 to 84.9%, while further increasing the NaOH concentration did not affect the desorption efficiency as illustrated in Fig. 7a. It can be also seen in Fig. 7b, that magnesium ferrite magnetic BC can achieve more than 25% desorption efficiency using 0.5 M NaOH after 10 adsorption/desorption cycles. However, due to the strong chemical bonding between phosphate and Mg/La modified BC [109,123], the phosphate ions were not easily desorbed by NaOH. For instance, the NaOH concentration was increased to 3 mol/L to achieve

high phosphate desorption efficiency from Mg-laden BC [108] and La-modified BCs [121,122].

The addition of NaCl to NaOH as an eluting agent for phosphate desorption was also reported for BCs regeneration. The NaOH is used for decreasing the adsorption capacity of phosphate while NaCl is targeted to desorb the phosphate ions by ion exchange. For example, Xu et al. [127] found that the addition of NaCl to NaOH significantly enhanced the desorption efficiency of the La modified BC. Their results also demonstrated that HCl has a lower desorption efficiency than the NaOH, which is in compliance with the previous discussions.

In general, it can be concluded that higher desorption efficiency can be achieved with NaOH solutions compared to other desorption solutions. However, most studies have reported only a very limited number of desorption cycles. Future research should focus on studying the regeneration, recovery and the real-life time (i.e. adsorption/desorption cycles) of the available and new fabricated adsorbents, which is important in providing a cost benefit analysis of the adsorbents.

6.2. Phosphate loaded BCs for agricultural applications

Since BCs are rich in carbon and nutrients, they have been used for soil amendment to enhance water retention, to increase the binding capacity of nutrients, improve soil fertility, plant growth and improve the water holding capacity of soil [149]. These benefits of BCs can contribute towards ecofriendly and sustainable agriculture [150].

Phosphate loaded BCs have been suggested for use in agricultural applications given that the regeneration of BCs is not often easy after adsorption [47,84]. As such, Yao et al. [51] recommended the use of phosphate laden sugar beet tailings BC as a fertilizers instead of regeneration of the adsorbent. The bioavailability of phosphate onto the exhausted BCs and phosphate delivery to the grown plants depending on different factors such as, the amount of phosphate that is already found in the structure of the BC, the adsorbed amount of phosphate onto the BC, the interaction between the laden phosphate and other nutrients in the BC that might be added from other sources, and it also depends on the interaction between phosphate and the available elements on the engineered BCs [72]. Different researchers have utilized the exhausted BCs as slow release fertilizers for plant growth [55,73,112,145]. In this regard, the phosphate laden BCs have been successfully used as slow release fertilizers for the growth of black gram seeds [43], maize seedlings [72], Chinese brassica [74], ryegrass plants [111], rice [117] and Lettuce leaves [112,137].

BCs and modified BCs were successfully applied for soil amendment, enhancing soil fertility and carbon sequestration [151]. Despite the successful progress that has been made using the phosphate laden BCs (the exhausted BCs that were used for phosphate removal) as slow release fertilizers, the phosphate releasing rate from the different BCs requires further investigation. Yao et al. [71,145] and Wan et al. [137] suggested that the effect of the slow released phosphate from the exhausted BC on plants growth can be evaluated by bioassay during the first stages of seedling growth. For instance, the assay results of Wan et al. [137] found that after 12 days of growth, the lettuce seedlings were greener, stronger and having more length than the controlled environment which was attributed to the phosphate released from the exhausted BC. Jung et al. [47], obtained larger leaf size and area in the first 30 days for phosphate laden BC than the plants grown in a commercial compost. Some researchers investigated the phosphate release from exhausted BCs by studying the phosphate leaching from these BCs with time, for example; Chen et al. [73], obtained a leaching rate of 0.64 mg/g in 88 h from a montmorillonite/BC composite holding a phosphate of 105.28 mg/g. Yao et al. [145] obtained a release rate of 4.5 mg/g in 144 h from Mg-enriched tomato tissues BC holding 116.6 mg/g of phosphate. However, further experimental work, theories, modelling and technologies are required to study and monitor the phosphate release from exhausted BCs into plants. Furthermore, safety issues and the immobilization of loaded metal ions into the soil and plants requires deep

investigation. In addition, proper policies/guidelines are needed to control such application of BCs.

7. BCs for phosphate removal from actual wastewaters

To date, most of the studies on phosphate remediation from water by BCs are lab scale experiments. The majority of these studies have investigated the performance of BCs in synthetic water that contains only spiked solution of salts of phosphoric acid. Only a few studies have tested the BCs for phosphate removal from actual wastewaters and other natural water bodies [81,108,129,141]. It should be noted that phosphate removal from wastewater streams is affected by organic/inorganic species content, bacterial component presented in the wastewaters and other contaminants. Several studies found that the removal of phosphate from wastewater is more complex than the simple testing of adsorbents in synthetic waters [104]. This is usually attributed to the competition between phosphate and other contaminants on the vacant active adsorption sites, the interaction between phosphate and other organic matters found in the actual streams and the potential blockage of adsorbent pores by biological and organic contaminants [12,13]. Some of the studies found that modified BCs have shown high phosphate removal from wastewaters and natural waterbodies such MgO-impregnated BC [110] and CaO-MgO hybrid BC [74]. However, there is a lack of data on phosphate removal from actual wastewater streams by unmodified and modified BC and this should be one of the next steps of future research in phosphate removal by BCs.

8. Conclusions

In this review, the recent studies on the adsorptive removal of phosphate from aqueous solutions by using both unmodified and modified BCs have been summarized and discussed. BC preparation methods, pyrolysis conditions, BC feedstock, BC surface properties, experimental adsorption conditions, optimum pH of phosphate removal, isotherm, kinetics and maximum phosphate adsorption capacities were reviewed. Furthermore, adsorption thermodynamics, mechanisms, the effect of coexisting ions, desorption of phosphate and possible use of phosphate laden BCs for agricultural applications were also considered.

The removal of phosphate from water was found to be spontaneous and endothermic for most of the prepared BCs. The adsorption capacity of unmodified BCs towards phosphate depended on the mineral content and the surface properties of the BC. The unmodified BCs that demonstrated Ca and Mg ions within their structure have shown the highest adsorption capacity among the unmodified BCs. Regarding modified BCs, the BCs impregnated with Ca and Mg ions were found to possess a significant enhancement in phosphate adsorption capacity. In addition to Ca and Mg ions, Al, La and Fe were also used to dope BCs to enhance the phosphate removal from water. The highest reported phosphate loading onto BCs was 758.96 mg(P)/g found for Al modified sugar cane straw BC. It should be mentioned that proper comparison between the different BCs and their composites in terms of adsorption capacity towards phosphate is a challenging task due to the variety of experimental conditions and BCs feedstock's.

It is well documented in numerous studies that phosphate adsorption onto BCs is sensitive to pH of the feed solution and adsorption process is controlled by different mechanisms, such as electrostatic interactions, ion exchange, ligand exchange, Lewis acid base interactions, hydrogen bonding, inner and outer sphere complexation. Regarding the effect of competitive ions in the feed; it was shown that, carbonate anions has the highest negative impact on the phosphate removal. In terms of adsorbent regeneration, alkaline solutions using NaOH were the most efficient and often used for BCs regeneration.

It should be highlighted that phosphate laden BCs are rich in nutrients and can be applied as slow release fertilizers for soil enrichment. A number of studies on BCs application in land and soil enrichment is continuously growing. Despite many studies on phosphate removal with

BC have been performed over last decades, however, there are research gaps that need to be addressed:

- Though, Mg, Ca, Al, La and Fe were the most commonly used elements for BCs doping, however, proper comparison on the BC prepared from same feedstocks' treated with different elements are rather limited. Leaching of doping elements and real-life time of the adsorbents should also be evaluated.
- There is a lack of data for phosphate removal with BCs in complex multicomponent solutions. The effect of coexisting ions on phosphate removal was not studied in detail and should be addressed in future research.
- It should be outlined that all of the conducted research have been performed at lab scale and further scaling up of the experiments is needed. Moreover, very few studies have conducted the continuous flow removal of phosphate by BC and more focus must be given to column study investigations.
- There is a lack of data on phosphate removal (i) at low feed concentrations, (ii) from actual wastewaters and (ii) other natural water bodies. In addition, the selectivity of phosphate recovery against organic, inorganic and biological contaminants by BCs is not described in the literature.
- Despite the success of using some phosphate laden BC as slow release fertilizers, the phosphate releasing rate from BC into the soil has been not properly investigated and should be further addressed. In addition, there are knowledge gaps related to the environmental impact, safety issues and economic implications of such applications.

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.

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Appendix A. Supplementary data

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