Magnetic Activated Carbon Production from Lignin and Ferrous Salts

Process Modification for Enhanced Phosphate Adsorption from Aqueous Solutions

ZHAORAN ZHENG
Abstract

The treatment and control of superfluous aqueous phosphate is a critical task in environmental management. Magnetic bio-activated carbon is a good adsorbent for physical adsorption methods with several environmental and economic advantages. A streamlined and new method for production of magnetic bio-activated carbon from lignin is finished and presented by Tong Han. To enhance the phosphate adsorption and find the optimization process for mac production from lignin, it’s necessary to investigate influence of process parameters on the quality of the final products systematically. In this work, four different modification of process are used to investigate the influence of process parameters on the quality of the final products systematically, which shows how the proportion of iron oxides, the dispersion of iron oxides and the degree of activation influence the capacities. And the maximum capacity is around 50mg/g, which is a relatively high improvement.

Key word: Magnetic bio-activated carbon, phosphate adsorption, lignin, steam activation.

Sammanfattning

Behandling och kontroll av överflödigt vattenhaltigt fosfat är en kritisk uppgift i miljöhantering. Magnetiskt bioaktivert kol är ett bra adsorbent för fysiska adsorptionsmetoder med flera miljömässiga och ekonomiska fördelar. En strömlinjeformad och ny metod för produktion av magnetiskt bioaktivert kol från lignin är färdig och presenteras av Tong Han. För att förbättra fosfatadsorptionen och hitta optimeringsprocessen för mac-produktion från lignin är det nödvändigt att systematiskt undersöka påverkan av processparametrar på kvaliteten på de slutliga produktarna. I detta arbete används fyra olika modifieringar av processen för att systematiskt undersöka påverkan av processparametrar på slutprodukternas kvalitet, vilket visar hur andelen järnoxider, spridningen av järnoxider och graden av aktivering påverkar kapaciteten. Och den maximala kapaciteten är cirka 50 mg/g, vilket är en relativt hög förbättring.

Nyckelord: Magnetiskt bioaktivert kol, fosfatadsorption, lignin, ångaktivering
# Table of content

1. Introduction ............................................................................................................. 1
2. State of Art .............................................................................................................. 5
   2.1 Previous work ................................................................................................... 9
   2.2 Objective ....................................................................................................... 9
3. Experimental ......................................................................................................... 11
   3.1 Synthesis of the Magnetic Bio-activated Carbons .................................. 11
   3.2 Characterization ...................................................................................... 12
   3.3 Phosphate adsorption measurement ........................................................ 12
4. Results and discussion .......................................................................................... 14
   4.1 Characterization of the produced MACs ............................................... 14
      4.1.1 Pore structure ................................................................................ 14
      4.1.2 Iron content and iron forms .......................................................... 14
   4.2 Adsorption of phosphate ........................................................................ 16
   4.3 Social and ethical aspects ........................................................................ 19
5. Conclusion ............................................................................................................ 20
6. Further contribution .............................................................................................. 21
7. Acknowledgments ................................................................................................. 22
8. Reference .............................................................................................................. 23
1 Introduction

The treatment and control of superfluous aqueous phosphate is a critical task in environmental management because of the disadvantageous effects of aqueous phosphate on body health and natural ecosystems whether in the short or long term [1]. No bionetwork or living creature can survive without clean water, which is one of the most common resource on Earth. There is three-fourths of the Earth's surface being covered with water approximately [2]. However, 97% of the total water source is contained in the ocean and other salty bodies. Thus, it’s difficult to use for most purposes directly [3]. And also, it has been reported that of the remaining 3% of water, around 2.4% is bound in glaciers, ice caps, atmospheric and soil moisture, which is making it unreachable for daily use [2]. Thus, humans have to depend on the remaining approximately 0.6% of the global fresh water resources found in rivers, lakes, and groundwater [4].

The radical increase in the release of pollutants into aquatic ecosystems has contributed widely to the continuing worsening of the quality of available freshwater resources [5]. As is well known, phosphate ($PO_4^{3-}$) is an essential nutrient, but its abundance can lead to eutrophication in many aquatic systems [6] [7]. Natural sources of aqueous phosphate contain the decomposition of rocks and minerals, sedimentation, erosion, atmospheric deposition, stormwater runoff and direct input by flora and fauna [6] . The major anthropogenic sources of aqueous phosphate are industrial discharge, release from wastewater treatment facilities, and agricultural runoff [7]. The discharge rate of phosphates into aquatic environments has enlarged in response to continuous rises in human activities. Consequently, the severe environmental worries related to phosphate pollution have become an important subject for research and development [7]. The number of publications associated with the adsorptive removal of extra phosphate from aquatic environments has been growing gradually.

Raised levels of phosphate in water bodies can rise the costs of water treatment and reduce the recreational value of watercourses by generating threatening algal blooms. Such algal blooms generally produce cyanotoxins that pose main health risks and lead to an odor annoyance to the neighboring community [8]. The redundant use of phosphate resources for the production of chemical manures and wide phosphorus (P) runoff from agricultural activities have raised phosphate levels in surface watercourses [9]. The abundance of phosphate facilitates the overgrowth of algae and plants [1] [8]. The bacterial decomposition of biomass caused by algal death spends large amounts of oxygen in the water bodies, which leading to a state of hypoxia in the ecological systems [10]. Thus, eutrophication can lead reduction of dissolved oxygen content and cause the formation of toxins which harm aquatic flora and fauna, chiefly in shallow...
lakes, estuarine, and coastal marine areas [8]. Phosphate is a vital chemical for plant development and can be the main limiting factor for the growth of plants in many water bodies [11]. Hence, irrepressible algae development could be ensued by keeping the concentration of phosphate as low as 0.02 mg/L [12].

Surface runoff and emissions are two common and significant ways by which harmful substances go in water ecosystems. Energetically controlling the removal of dangerous pollutants at their source could promote the effective protection of the environment. For example, phosphorus manure discharge is one of the principal contributors to the increase in aqueous phosphate concentrations globally [13]. The main components of ammoniated phosphorus fertilizer are monoammonium phosphate, diammonium phosphate, phosphoric acid, super phosphoric acid, and granulated triple phosphate [14]. It has been valued that over than 40 million tons of phosphorus chemical manures are spent worldwide every year [14]. As a regulatory measure, the United States Environmental Protection Agency has forced a limit of 0.025 mg/L of phosphate in tanks used for drinking water [15].

Natural storage of phosphorus is limited and is expected to be depleted the course of the next 50 years due to exponential growing in the use of phosphate fertilizer for agronomic advances [16] [17]. Consequently, many recent researches have pay attention to developing new technologies to both hinder eutrophication and address the global dilemma of phosphorus lack [17]. Recovering phosphorus from phosphate-boosted water bodies has been extensively appreciated as a key and new strategy to address phosphorus lack [18]. Different chemical, physical, and biological methods have been established and used widely in numerous applications to develop regulatory measure and treatment techniques for aqueous phosphate [19] [20] [21]. Among them, adsorption by different absorbents (e.g., zeolite, carbon nanotubes, and activated carbon) has proved to be a workable alternative because of its high selectivity and simple operation. However, those options have some economic and technical shortcomings such as low renewability, undesirable adsorption capabilities and need for careful discarding after use [22] [23].

Accompanied by conventional porous materials, biochar, a carbonaceous solid material manufactured from biomass pyrolysis at high temperature under a low oxygen atmosphere, has lately attracted important scientific interests due to its the extensive availability of the essential feedstock, relatively large specific surface area, and its highly porous structure, low-cost, and stable carbon matrix [24] [25]. The structural flexibility of biochars and simple fabrication guarantee the efficient absorptive removal of pollutants from water bodies [25].

Up to now, several different methodologies have been expressed for the extenuation of aqueous phosphate such as anion exchange membranes [26], chemical precipitation involving alums and ferric ions. Generally, chemical precipitation is the most
commonly used method, nevertheless it is limited by the generation of huge amounts of sludge [20] [21]. These methodologies have been improved biological uptake [27] and adsorption [28]. Anyhow, it remains necessary to minimize aqueous phosphate concentration to very low values since huge amounts in aqueous systems can cause wide eutrophication.

Industrial-scale exercises for the removal of pollutants from waste watercourses are often heavily reliant on fixed-bed filtration systems [22]. To optimize fixed-bed filtration operations, there are many designed mathematical models describing the transfer and fate of pollutants [29]. To prevent pollutants from advancing along the waste water streams, Fixed-bed filtration systems often use porous adsorbents as packing media. For purpose of optimizing the treatment process, laboratory-scale columns filled with porous media are used to authenticate mathematical filter equations (e.g., advection-dispersion equation–based models) [30]. These equations confirm the removal of heavy metals using biochar in aqueous systems and influence further research and development of other water contaminants [30]. However, most formerly developed technologies are high cost and require high energy or many chemical processing [22]. Thus, novel technologies that use stable and ecofriendly materials with low cost processing, improved energy efficiency, and reusability are required.

Many sorbents have been developed and are used together with many of the aforementioned technologies due to their simplicity, relatively low cost, and feasibility under surrounding conditions [28]. On the strength of target pollutant of an adsorbent and its physical structure, a solid adsorbent can be engineered for desired adsorption. In the last few decade, various adsorbents, including activated carbon, zeolite, and metal oxides, have been used for several wastewater control and treatment techniques [26]. Fascinatingly, activated carbon has been presented as the most normally used sorbent for the elimination of a wide array of contaminants from water, including phosphate, owing to its mechanically strong properties, highly porous structure, and non-connection with chemical waste products [24]. Adsorbents have been impregnated with metal hydroxides (oxides), transition metal ions, and other chemicals to improve their elimination capacity for aqueous phosphate [31] [32]. Notwithstanding, some report are successful, traditional adsorbents are troubled in disadvantages, such as low renewability, high cost (Table 1 [33]), and difficult disposal after use. Consequently, traditional adsorbents are seldom used for extensive practical applications.
<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Type</th>
<th>Particle size</th>
<th>Density (g/ml)</th>
<th>Cost ($/100 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite</td>
<td>Silver-exchanged</td>
<td>&gt;20 mesh</td>
<td>1.07</td>
<td>592</td>
</tr>
<tr>
<td>Zeolite</td>
<td>Silver-exchanged</td>
<td>&gt;20 mesh</td>
<td>1.07</td>
<td>514</td>
</tr>
<tr>
<td>Zeolite</td>
<td>Linde Type A</td>
<td>-</td>
<td>-</td>
<td>292</td>
</tr>
<tr>
<td>Zeolite</td>
<td>Faujasite Type</td>
<td>-</td>
<td>-</td>
<td>292</td>
</tr>
<tr>
<td>Zeolite</td>
<td>Ammonium Y</td>
<td>-</td>
<td>-</td>
<td>85</td>
</tr>
<tr>
<td>Activated charcoal</td>
<td>Acid-washed</td>
<td>-</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>(hydrochloric acid)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated charcoal</td>
<td>Acid-washed</td>
<td>-</td>
<td>-</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>(hydrochloric acid)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated charcoal</td>
<td>Gas chromatography</td>
<td>0.3–0.5 mm</td>
<td>0.4-0.5</td>
<td>178</td>
</tr>
<tr>
<td>Activated charcoal</td>
<td>Gas chromatography</td>
<td>0.3–0.5 mm</td>
<td>0.4-0.5</td>
<td>135</td>
</tr>
</tbody>
</table>
2 State of Art

As a novel type of porous materials, biochar has recently been focused as a next generation sorbent for the removal of aqueous phosphate [34] [35]. Biochars are considered by high surface areas, structural flexibility, stable carbon matrix, easy fabrication, and high porosity [35]. What’s more, biochars are low-priced and have less energy requirements for their production than traditional adsorbents, such as activated carbon, which requires raised temperatures and additional activation processes [36]. Moreover, biochars can be produced from various biomass categories, particularly from low-cost wood biomass, agricultural biomass, solid waste, and animal litter, via different thermochemical processes (e.g. hydrothermal carbonization fast pyrolysis, slow pyrolysis, torr faction, flash carbonization and gasification) [37]. Consumed biochar can also be successfully used for soil remediation, therefore offering a supportable environmental management approach, which is not the case for conventional adsorbents [24]. Additionally, translating invasive plant species, such as certain marine algae or water hyacinth, into biochar has been extensively acknowledged as an operative environmental protection plan [38]. Thus, biochar has several environmental and economic advantages and is being investigated widely for the removal of additional aqueous phosphate. Nevertheless, biochars still have limit in its practical applications for water control and treatment compared to activated carbon due to its limited surface area and poor mechanical properties [24]. Moreover, neither biochar nor activated carbon have good performance in recycle.

To enhance efficiency of recycle and reuse, magnetism is a good considered property, which is easy to separate biochar/ activated carbon from treated waste water by giving biochar/ activated carbon magnetic property. According to the magnets contained, there are mainly three kinds of magnetic activated carbon “iron-based, cobalt-based, and nickel-based”. Compared with other magnetic elements such as cobalt and nickel, Fe is abundant, low price, safe and non-toxic, and is most widely used in the preparation of magnetic activated carbon.

Besides the advantage of being easily recycled from a system using a magnet, magnetic biochars/bio-activated carbons, which are produced by adjusting biochar / bio-activated carbon with iron oxide particles, have been confirmed to own much higher phosphate adsorption capacities than conventional biochars or bio-activated carbons. The major cause is that the electrostatic attraction between metal oxides and phosphates could be suggestively improved [39].

The preparation of magnetic activated carbon is mainly focused on two-step process, which is based on the finished activated carbon. To get carbon/magnetic composite materials, the magnetic material (or precursor) is combined with the activated carbon.
in a "physical-mechanical" method with bonding, milling, adsorption, chemical coprecipitation or secondary activation. Among them, the adsorption method, the chemical coprecipitation method are the most reported. The adsorption method is based on the preparation of the magnetic fluid. The activated carbon is immersed in the solution containing the magnetic fluid and continuously stirred, and the excess magnetic fluid is removed by pickling or ultrasonication. Thus, magnetic activated carbon is obtained. At present, the magnetic fluids used in the adsorption method are mainly reported by $Fe_3O_4$ [40] and $\gamma-Fe_2O_3$ [41]. The preparation of the magnetic fluid $Fe_3O_4$ is mainly used coprecipitation method. The steps are shown as follows: Fe (III) and Fe(II) salts are prepared into a solution with a certain ratio. Then ammonia or sodium hydroxide is added as precipitant. Chemical coprecipitation method of involves first immerses the finished activated carbon in a mixed solution Fe (III) and Fe (II) salt, so that Fe$^{2+}$ and Fe$^{3+}$ infiltrate or adsorb in the pores of the activated carbon, and then change the pH to obtain iron hydroxide. Increase the temperature, in order that the iron hydroxide is converted into an iron oxide. Thus, the magnetic activated carbon with magnetic particles is obtained. However, both of two methods applies magnetic particles to the finished activated carbon, so the pores of the magnetic activated carbon are also easily blocked. These processes unavoidably cause the extra energy and time consumption. Furthermore, complex waste, principally referring to polluted water, is also unavoidably to be produced after chemical co-precipitation or impregnation processes [42]. Additionally, both chemical co-precipitation and impregnation methods lead to the formation of magnetic particles on the surface of biochar. In this way, the efficiency of combination between carbon and iron oxides is relatively loose. In a word, a streamlined process for magnetic biochars or magnetic activated carbons with high porosity generation and strongly embedded iron oxides is still needed.

Lignin is the second most rich natural raw material [43] and most abundant natural aromatic polymer [44], whose major function is a kind of adhesive for cellulose fibers in plants. The molecular model of lignin with molar mass of 1692 is shown in Fig. 1. It is usually obtained from black liquor, a waste production discharged from paper plants with large amounts, and which can result in a major problem of disposal [45]. Conversely, as the production of lignin quantities to more than 50 million tons per year there has been growing interest in the development of economically practicable novel examples and applications can be searched on the website of the International Lignin Institute [46]. At present, much of the lignin produced by the paper industry is distributed as a fuel. Even though there are some other applications on the edge, such as tanning agent or adhesive, no main large-scale application has so far been originated [43]. Another possible application for additional lignin is as a raw material for biochar / activated carbon (AC) production. Actually, since lignin has a molecular structure like bituminous coal and relatively high carbon content, it should be an ideal raw material.
What’s more, large amounts of researches that are presently available confirm that lignin is a principally interesting material to use.

Fig. 1 Molecular model of lignin with molar mass of 1692, containing nine guaiacol units.  
White = H; gray = C; black = O [63]

In fact, to enhance the performance (surface area and poor mechanical properties) of biochar, secondary activation is often accepted method for a biochar that need to be optimized. Thus, the bio-based activated carbons (BACs) often have advantages belong to both biochar and traditional activated carbon (e.g. environmental-friendly, high surface area and good poor mechanical properties).

As lignin is abundant in carbon content and has a proven ability for sorption, it is a good alternative for the production of ACs. Various activation methodologies have been expressed for production of lignin based ACs, such as physical method and chemical method. Generally, physical method is implemented by \( \text{CO}_2 \) or steam at high temperature and Chemical method is applied by \( \text{ZnCl}_2 \), KOH and phosphoric acid. A brief summary of the work is shown in table 2.
<table>
<thead>
<tr>
<th>Activation</th>
<th>Conditions</th>
<th>Surface area (m²/g)</th>
<th>Micropore volume (cm³/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical: carbonization– N₂</td>
<td>C (300 °C, 1 h)</td>
<td>&lt; 10</td>
<td>&lt; 0.01</td>
<td>[47]</td>
</tr>
<tr>
<td>Physical: carbonization– N₂</td>
<td>C (350 °C, 1 h) + A (800 °C, 40 h)</td>
<td>1613</td>
<td>0.47</td>
<td>[48]</td>
</tr>
<tr>
<td>Activation– CO₂</td>
<td>C (350 °C, 1 h) + A (850 °C, 20 h)</td>
<td>1853</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>Physical: carbonization– N₂</td>
<td>C (500-900 °C)</td>
<td>10-50</td>
<td>-</td>
<td>[49]</td>
</tr>
<tr>
<td>Physical: carbonization– Ar activation – steam</td>
<td>C (600 °C, 2 h) + A (800 °C)</td>
<td>865</td>
<td>0.365</td>
<td>[50]</td>
</tr>
<tr>
<td>Physical: pyrolysis (fluidized bed) – air (with Al–Cu–Cr catalyst) activation– steam</td>
<td>pyrolysis – (700 °C) A (780°C)</td>
<td>769</td>
<td>-</td>
<td>[51]</td>
</tr>
<tr>
<td>Physical: steam activation</td>
<td>700 °C, 2 h</td>
<td>-</td>
<td>0.33</td>
<td>[52]</td>
</tr>
<tr>
<td>Chemical: carbonized then activated with KOH</td>
<td>Lignin: KOH= 4:1 700 °C, 1 h</td>
<td>514</td>
<td>0.214</td>
<td>[47]</td>
</tr>
<tr>
<td>Chemical: ZnCl₂, H₃PO₄, K₂CO₃, Na₂CO₃, KOH, NaOH</td>
<td>Impregnation ratio 1 for all</td>
<td>800–2000</td>
<td>-</td>
<td>[49]</td>
</tr>
<tr>
<td>Chemical: ZnCl₂</td>
<td>Lignin: ZnCl₂ = 1:2.3 (500 °C, 1 h)</td>
<td>1800</td>
<td>1.039</td>
<td>[53]</td>
</tr>
<tr>
<td>Chemical: H₃PO₄</td>
<td>Lignin: H₃PO₄ = 1:2 (427 °C, 1 h)</td>
<td>1459</td>
<td>0.82</td>
<td>[54]</td>
</tr>
<tr>
<td>Chemical: KOH</td>
<td>Lignin: KOH = 1:4 (850 °C, 15min)</td>
<td>2753</td>
<td>1.37</td>
<td>[55]</td>
</tr>
</tbody>
</table>

(*C: Carbonization, *A: Activation)
2.1 Previous work

To enhance phosphate adsorption capacity and recycling performance, bio-activated carbons produced with iron oxide particles is an excellent alternative. The use of lignin as a precursor to produce activated carbon signifies a capable method. The previous study express that a linear amorphous structure is leading in the lignin produced from pulping processes, which causes that such lignin often undergoes glass transition. Thus, such lignin can be softened and melted at temperatures ranging from 150 to 250°C while it is under a heat treatment [56], which causes a uniform flow state. In this way, iron salts can be primely dispersed in a homogenous lignin phase under heat treatment during melting when lignin is premixed with iron salts. After the carbonization and activation processes, lignin-based magnetic activated carbon with well-dispersed iron oxides can be produced. Particularly, the iron valence can be modified by picking different activation reagent because iron can also react with ordinary activation agents such as steam [57]. According to the above expounds, as shown in Fig. 2, a streamlined and new method for production of magnetic bio-activated carbon (MBAC) from lignin is finished and presented by Tong Han [58].

![Fig. 2 Process for production of magnetic activated carbon from lignin [58]](image)

2.2 Objective

As mentioned before, a novel and streamlined process to produce magnetic activated carbon from lignin has been proposed by Tong. The current work is the continuation of the previous work. The influence of process parameters on the quality of the final products is systematically investigated. The overall aim is to find the optimization
process for mac production from lignin. According to the above expounds of introduction, exposed iron oxide offers an electrostatic attraction with phosphate, which is an important adsorption property. Logically, relative high content of exposed iron oxide in produced magnetic carbon should lead to the positive change of adsorption capacity. To enhance the amount of exposed iron oxide, it is a direct approach that raise the total content of iron oxides in biochar by increasing iron slats in precursor before carbonization. Empirically, during steam activation, the exposed possibility of iron oxide should increase with homogenous dispersion of iron in biochar which is produced after carbonization. And different mix methods of precursors can cause different dispersion of iron oxides in produced MACs. In addition, the high activation degree of MAC means that high mass loss of carbon and more exposed iron oxide, which decided by larger steam/biochar ratios. Thus, the proportion of iron oxide, the dispersion of iron oxides and the degree of activation are interested factors via process modification with different content of iron slats, premixed method and amount of activation agent (steam) in this work.
3 Experimental

Lignin is the carbon source in this work, and it has been isolated from a pulping process. Practically, the lignin (Kraft lignin) is isolated from spruce as stated by the Clean Flow Black process [59]. The lignin was dried at room temperature and reached a constant moisture content of around 2% before being used. Afterwards, it was sieved to make finest particles smaller than 0.125 mm. FeSO$_4$, which was bought from Sigma-Aldrich, was played a role as the magnetic component precursor. The ferrous sulfate was milled and sieved before the experiment. The size range of lignin and ferrous salt is similar (< 0.125 mm). $KH_2PO_4$, which was also bought from Sigma-Aldric, is guaranteed reagent grade to ensure the precision.

3.1 Synthesis of the Magnetic Bio-activated Carbons

The iron content of the MAC precursor with lignin and ferrous sulfate is approximately 8%, which is twice times than MACs produced by Tong [56]. 10 g of lignin and 3.8 g of FeSO$_4$ were mixed by two approach, i.e. mechanistical mix and wet impregnation, to get different the dispersion of iron salts. Thereafter, the samples were placed in a silica boat container. Then, the silica boat container filled with the sample was positioned in the tubular electric furnace. In the meantime, nitrogen at a flow rate of 50 ml/min was replenished. Samples were heated to 250°C and kept for 20 min to ensure completely lignin melting. Afterwards, the samples were supplementary heated to 800°C which is the final carbonization temperature. The heating rate and duration time of the furnace were 10 °C/min and 1 h which were the same for all cases.

The produced biochars were further activated at 800°C with steam to produce the magnetic bio-activated carbon in the present work. Initially, the produced biochars were put in the designed container. The flow rate of nitrogen was of 50 ml/min during the heating process, nevertheless the nitrogen was changed to steam as soon as the furnace temperature reached 800°C. Two steam/biochar ratios (wt./wt.), i.e., 4 and 8, were selected to reach a different degree of activation. The produced MBACs are labeled as table 3. During the whole activation process, the amount of steam which reacts with every unit of biochars in the same period of time was fixed. In addition, the different steam/biochar ratios were set by altering the activation time.
Table 3 Label of MACs

<table>
<thead>
<tr>
<th>Label of MACs</th>
<th>Mix method</th>
<th>steam/biochar ratios (wt./wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mechanistical Mix</td>
<td>Wet Impregnation</td>
</tr>
<tr>
<td>MAC 1</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>MAC 2</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>MAC 3</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>MAC 4</td>
<td>×</td>
<td>×</td>
</tr>
</tbody>
</table>

(× represents the selection of methods)

3.2 Characterization

The textural properties of the MACs were determined by nitrogen adsorption-desorption isotherms at 77 K with a Micromeritics model ASAP 2000 instrument. The surface areas were calculated based on the BET equation, and the micropore surfaces were attained by using the t-plot method, while the pore volumes and pore size distributions in the mesopore ranges were obtained based on density functional theory (DFT) calculations. The pore size distribution in the micropore range was obtained by the Horvath and Kawazoe (HK) method.

The iron contents of the MACs were determined by applying an ICP-AES instrument. Throughout the measurements, the samples were first dissolved with a microwave digestion instrument and positioned in the ICP-AES instrument to determine the iron content after that.

XRD was aimed at detecting the crystal form of the iron species in the MACs. The XRD patterns were measured by applying a Siemens D5000 diffractometer and a monochromatic Cu Kα radiation source (30 mA, 40 kV). Intensities were set in the range of 10 to 90° with a step size of 0.02 °/s.

3.3 Phosphate adsorption measurement

Solutions with different phosphate concentrations (5 mg/L, 10 mg/L, 25 mg/L, 50 mg/L, 100 mg/L, 500 mg/L, 1500 mg/L, 3000 mg/L) were set by dissolving a specific amount of $KH_2PO_4$ in deionized water, and the initial pH was adjusted to 7 using 1 mol/l NaOH.
For all phosphate adsorption tests, 0.4 g of the selected MAC sample was put to 60 ml phosphate solutions. Each experiment had at least three replicates. The mixtures were mechanically agitated for 24 h at room temperature. The phosphate concentration in the filtrates was measured with a total phosphorus detector. [60]
4 Results and discussion

4.1 Characterization of the produced MACs

To investigate influence of process parameters on the quality of the final products systematically, pore structure, iron content and iron forms are most interested.

4.1.1 Pore structure

As is shown in Table 4, both MAC1 and MAC3 are provided with lower mesopore volume than magnetic carbon produced by Tong with same activation degree, i.e., steam/biochar ratios of 4. [56]. It ought to be that iron is an inhibitor during activation process. MAC1 possesses the highest surface area and relatively low mesopore volume. On the contrary, MAC3 has lowest surface area and highest mesopore volume. According to mathematic knowledge, the mesopore volume were higher, the surface area is lower. Mesopore volume and surface area is the most interested result in this work because they are the main factors in phosphate adsorption [56]. For the MACs with different degree of activation by using same mixing method, the total pore volume and mesopore volume are increase obviously with rise of steam/biochar ratios. Along with the activation process, the micropores can grow up because of the further reaction between biochars and steam. However, it’s difficult to judge how the dispersion of iron oxides influence the pore structure of MACs.

<table>
<thead>
<tr>
<th></th>
<th>MAC1</th>
<th>MAC2</th>
<th>MAC3</th>
<th>MAC4</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m²/g)</td>
<td>645.83</td>
<td>543.24</td>
<td>379.84</td>
<td>586.88</td>
</tr>
<tr>
<td>Total pore volume (cm³/g)</td>
<td>0.3704</td>
<td>0.2978</td>
<td>0.4842</td>
<td>0.5288</td>
</tr>
<tr>
<td>Micropore volume (cm³/g)</td>
<td>0.2628</td>
<td>0.217</td>
<td>0.1633</td>
<td>0.2397</td>
</tr>
<tr>
<td>Mesopore volume (cm³/g)</td>
<td>0.1076</td>
<td>0.0808</td>
<td>0.3209</td>
<td>0.2891</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>2.2943</td>
<td>2.1928</td>
<td>5.0992</td>
<td>3.604</td>
</tr>
</tbody>
</table>

4.1.2 Iron content and iron forms

The iron content of the produced MACs was measured with the ICP-AES technique. The result is shown in Table 5. It can be seen the iron content of MAC4 is more than two times than others.
Table 5 Iron content

<table>
<thead>
<tr>
<th></th>
<th>MAC1</th>
<th>MAC2</th>
<th>MAC3</th>
<th>MAC4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron content wt.%</td>
<td>17.07</td>
<td>15.68</td>
<td>16.8</td>
<td>41.17</td>
</tr>
</tbody>
</table>

\[
C_{Fe} = \frac{W_{FeSO_4} \times (1 - C_{H_2O}) \times \left(\frac{M_{Fe}}{M_{FeSO_4}}\right)}{W_{FeSO_4} + W_{lignin}}
\]  

(1)

Where \(C_{Fe}\): the content of iron of initial mixture;  
\(C_{H_2O}\): the water content of the raw \(FeSO_4\) sample;  
\(M_{Fe}\): the molecular weight of iron;  
\(W_{FeSO_4}\): the weight of the raw \(FeSO_4\) sample (including crystal water);  
\(W_{lignin}\): the weight of the raw lignin materials

According to equation (1), the iron content of the initial mixture of lignin and \(FeSO_4\) can be calculated and result is approximately 8%. Table shows that the total mass loss increases with rise of activation degree. If there is not any iron loss during the process, the calculated content of iron (based on equation 2) shown in Table 6 is higher than final result shown in table 5. According to previous works, there is almost no iron was lost during the steam activation process [56]. The reason why calculated content of iron is lower ought to be that the iron was drained out with the volatiles during carbonization and. It can be judged that the total mass loss rate of the mixture of ferrous salt and lignin is much higher than iron loss rate at carbonization. The main reason should be that ferrous salts were surrounded in the molten lignin.

Table 6 Mass loss of MACs

<table>
<thead>
<tr>
<th></th>
<th>MAC1</th>
<th>MAC2</th>
<th>MAC3</th>
<th>MAC4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Mass Loss (%)</td>
<td>62.5</td>
<td>73.7</td>
<td>70.0</td>
<td>83.1</td>
</tr>
<tr>
<td>(C_{Fe}^{*}) (wt. %)</td>
<td>21.3</td>
<td>30.4</td>
<td>26.7</td>
<td>47.3</td>
</tr>
</tbody>
</table>

\[
C_{Fe}^{*} = \frac{C_{Fe}}{1 - M_{loss}}
\]  

(2)

Where \(C_{Fe}\): the content of iron of initial mixture, i.e. 8%;  
\(C_{Fe}^{*}\): the calculated content of iron if there is no iron loss;  
\(M_{loss}\): The total mass loss during carbonization and activation;

The crystal structure of the iron forms on the surface of the produced MACs was measured by applying a powder XRD instrument. The relevant XRD patterns are shown in Fig 3. The XRD patterns of the MACs confirm that the iron forms in all the produced
MACs mostly exist as desired $Fe_3O_4$, which offer a good magnetic property for MACs. Because iron is easily oxidized with steam to form magnetite, i.e. $Fe_3O_4$, during activation.

![Fig. 3 The XRD patterns of MACs](image)

### 4.2 Adsorption of phosphate

The Langmuir model assumes that the adsorption happens to monolayer onto a homogeneous surface without interactions between the adsorbed molecules and adsorbents [33]. The Freundlich model is an empirical equation, which are often employed to describe a behavior of chemisorption onto heterogeneous surfaces. For all equations, $q_e$ is the maximum adsorption capacity of the sorbents. $C_e$ represents the equilibrium solution concentration (mg/l) of the sorbate. The definition of parameters K, Q and n can be referred to the literature [61], and $R^2$ is correlation coefficient. The adsorption capacities of MACs are calculated by using equation 3, and the result are plotted as Fig. 4 to Fig. 7 above the table of adsorption model respectively. Langmuir and Freundlich equations were used to describe the experimental isotherms. As is shown in below figures and tables, all models reproduced the isotherm curve well with relatively high $R^2$ (more than 0.8). For the results of MAC1 and MAC3, although the correlation coefficients of Freundlich equations are larger than Langmuir, the parameters n of them are larger than 1, which is not fix the qualification of Freundlich equations (Freundlich equation requires 0<n<1). Thus, the Langmuir equation fits all of four experimental data and different parameters Q suggest what the maximum adsorption capacities of MACs are, respectively.
Isotherm data and modeling of phosphate adsorption on MAC1

![Isotherm data and modeling of phosphate adsorption on MAC1](image)

**Fig. 4 Isotherm data and modeling of phosphate adsorption on MAC1**

<table>
<thead>
<tr>
<th>Models</th>
<th>Formula</th>
<th>K</th>
<th>Q</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( q_e = \frac{K \cdot Q \cdot C_e}{1 - K \cdot C_e} )</td>
<td>6.993e-07</td>
<td>2.323e+04</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>( q_e = K \cdot C_e^n )</td>
<td>0.001499</td>
<td></td>
<td>1.303</td>
<td>0.9774</td>
</tr>
</tbody>
</table>

Isotherm data and modeling of phosphate adsorption on MAC2

![Isotherm data and modeling of phosphate adsorption on MAC2](image)

**Fig. 5 Isotherm data and modeling of phosphate adsorption on MAC2**

<table>
<thead>
<tr>
<th>Models</th>
<th>Formula</th>
<th>K</th>
<th>Q</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( q_e = \frac{K \cdot Q \cdot C_e}{1 - K \cdot C_e} )</td>
<td>0.002875</td>
<td>27.6</td>
<td></td>
<td>0.9261</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( q_e = K \cdot C_e^n )</td>
<td>0.8555</td>
<td>0.4305</td>
<td></td>
<td>0.8323</td>
</tr>
</tbody>
</table>
Isotherm data and modeling of phosphate adsorption on MAC3

![Fig. 6 Isotherm data and modeling of phosphate adsorption on MAC3](image)

<table>
<thead>
<tr>
<th>Models</th>
<th>Formula</th>
<th>K</th>
<th>Q</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_e = \frac{K * Q * C_e}{1 - K * C_e}$</td>
<td>5.438e-07</td>
<td>3.207e+04</td>
<td>0.9045</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>$q_e = K * C_e^n$</td>
<td>9.718e-07</td>
<td></td>
<td>2.24</td>
<td>0.9949</td>
</tr>
</tbody>
</table>

Isotherm data and modeling of phosphate adsorption on MAC4

![Fig. 7 Isotherm data and modeling of phosphate adsorption on MAC4](image)

<table>
<thead>
<tr>
<th>Models</th>
<th>Formula</th>
<th>K</th>
<th>Q</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_e = \frac{K * Q * C_e}{1 - K * C_e}$</td>
<td>2.819e-05</td>
<td>648.7</td>
<td>0.9957</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>$q_e = K * C_e^n$</td>
<td>0.03236</td>
<td>0.9178</td>
<td>0.9967</td>
<td></td>
</tr>
</tbody>
</table>
\[ q_e = \frac{(C_0 - C_e) \times V}{m} \]  

(3)

Where  
- \( q_e \): adsorption capacity  
- \( C_0 \): initial concentration of phosphate solution;  
- \( C_e \): concentration of phosphate solution after adsorption;  
- \( V \): solution volume, i.e. 60ml;  
- \( m \): mass of activated carbon, i.e. 0.4g;

Table 7 shows that the adsorption capacities of MACs in experiments with initial phosphate concentrations of 3000mg/L during 24h, which offers intuitive results to judge the degree of optimization. As is shown in the table 7, the adsorption capacities of MAC1, MAC3 and MAC4 are two times larger than MAC produced by Tong [56]. It ought to be two times content of iron oxide offers more electrostatic attraction to adsorb more phosphate in relatively high mesopore. The reason why MAC2 don’t have high adsorption capacity should be that the mesopore volume is relatively low which causing that there is not enough area to store phosphate.

However, as is shown table 5, the iron content of MAC4 is around three times as MAC1 and MAC3, but the adsorption capacity is similar. The reason ought to that adsorption capacity is decided by weak links of mesopore volume and content of iron oxide, which is a cask effect.

<p>| Table 7 Maximum capacities of MACs in experiments |</p>
<table>
<thead>
<tr>
<th>MAC1</th>
<th>MAC2</th>
<th>MAC3</th>
<th>MAC4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_e ) (mg/g)</td>
<td>48.63</td>
<td>24.73</td>
<td>52.23</td>
</tr>
</tbody>
</table>

### 4.3 Social and ethical aspects

The maximum capacity is a relatively important result to judge the ability of water treatment for an absorbent. For MACs in this work, most of them offer a relatively high maximum capacity comparing to other iron oxide magnetic activated carbon. The produced MACs are low cost and easy to mass production, which can be used in phosphate adsorption and reduce eutrophication in order to keep people healthy. What’s more, the iron form of MACs is magnetic iron oxide, which offer magnetism to the products. Thus, it is easy to separate MACs from treated water with a magnetic separation system. The used MACs ought to be recycled and reused after regeneration, which conform to sustainable development model.
5 Conclusion

In this work, four different modification of process are used to investigate the influence of process parameters on the quality of the final products systematically, which shows how the proportion of iron oxides, the dispersion of iron oxides and the degree of activation influence the capacities.

Increasing the proportion of iron oxides can cause the reduction of mesopore volumes, which may cause the lower rate of adsorption diffusion [62]. However, high proportion of iron oxides still enhance the phosphate adsorption, which express that electrostatic attraction offered by iron oxides is a significance factor of phosphate adsorption. It’s difficult to judge how the dispersion of iron oxides effect pore structure. For degree of activation, high level of activation degree gives biochar more mesopore, which increase the rate of adsorption diffusion. However, it is not a big influence of increasing phosphate adsorption in this work.

Obviously, increasing the proportion of iron oxides contribute to enhance phosphate adsorption and other factors doesn’t show enough evidence of raise the phosphate adsorption property. Generally, phosphate adsorption follows the cask effect of electrostatic attraction offered by iron oxides and the rate of adsorption diffusion decided by mesopore volume.
6 Further contribution

For steam activation, iron content is an important influence factor, which cause the different degree of activation and pore structure. To optimize the content of iron, the mechanism of activation should be focused. What’s more, Other activation methods such as KOH chemical activation and other metal oxide such as Mg may help to increase the phosphate adsorption.
7 Acknowledgments

The financial support from FORMAS, the Swedish research council for sustainable development are highly appreciated. Emphatically, thanks to Tong Han, Ph.D. candidate of KTH-Royal Institute of Technology, School of Industrial Engineering and Management Department of Materials Science Engineering, Group of Processes for helping authors designing experiments and analyzing results.
8 Reference


M. Inyang, B. Gao, Y. Yao, Y. Xue and A. Zimmerman, "Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass," Bioresource Technology, pp. 50-56, 4 2012.


Y. Xue, B. Gao, Y. Yao, M. Inyang, M. Zhang, A. Zimmerman and K. Ro, "Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: Batch and column tests," Chemical Engineering Journal, pp. 673-680, 15 8 2012.


[38] H. Zhang, C. Chengrong, E. Gray, S. Boyd, H. Yang and D. Zhang, "HMGB1 induced inflammatory effect is blocked by CRISPLD2 via MiR155 in hepatic fibrogenesis," Molecular Immunology, pp. 1-6, 1 2016.


[56] T. Han, N. Sophonrat, A. Tagami, O. Sevastyanova, P. Mellin and W. Yang, "Characterization of lignin at pre-pyrolysis temperature to investigate its melting


[60] HANGZHOU LOHAND BIOLOGICAL Co. Ltd., China.


