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Comparison between Chemical Modification of Biochar for Different Environmental Applications

Huiyi Tan[a], Chew Tin Lee[a], Keng Yinn Wong[b,*], Pei Ying Ong[a], Mohd Hafiz Dzarfan Othman[a], Kok Sin Woon[c], Guo Ren Mong[c]

[a]Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310, Johor, Malaysia
[b]Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia
[c]School of Energy and Chemical Engineering, Xiamen University Malaysia, Sepang, Selangor, Malaysia
kengyinnwong@utm.my

Biochar is a carbon-enriched product produced by thermochemical treatment of biomass under oxygen-deprived conditions. Its unique physicochemical properties have attracted considerable attention as a multifunctional material for various environmental applications. While biochar inherently possesses some pores and functional groups like carbonyl and hydroxyl groups, the amount is minimal compared to the bulk surface of biochar. The resultant physicochemical properties of biochar, including its surface morphology and functional groups, can be further improved through different chemical modification methods. This review aims to provide an overview of different chemical modification methods, including the activation using different acid and basic reagents, nanomaterial impregnation and magnetisation. Their effects on biochar's physicochemical properties, surface functionalities, and potential applications are explored. The enhanced properties of chemically modified biochar would have greater applicability in different applications, especially for pollutant removal, soil remediation and wastewater treatment. Future research should focus on improving the efficiency of modification processes and chemical recovery to prevent chemical wastage and produce biochar with desired characteristics for industrial-scale application. The integration of various chemical modification strategies with magnetization could produce biochar with enhanced surface functionalities and facilitate its recovery from aqueous environments.

1. Introduction

Biochar can be produced from a wide range of biomass, including sewage sludge, animal manure, agricultural and forestry waste through pyrolysis. This biomass would be the most ideal since they are non-hazardous, environmental-friendly, abundant and readily available in its natural environment (Shrivastava and Kumar, 2015). Biochar production is identified as a sustainable and low-cost technology that has received much attention in recent years due to the availability of cheap feedstocks and its excellent role in many environmental applications such as carbon sequestration, salt mitigation, heavy metal removal, greenhouse gas emission reduction, bioenergy production and waste management (Tan et al., 2023b).

The performance of biochar in different applications is mainly determined by its physicochemical properties. The surface area, porosity and amount of functional groups of biochar are the most crucial factors affecting its performance (Leng et al., 2021). Based on previous studies, biochar is characterised by high porosity, large surface area and abundant surface functional groups (Tan et al., 2022). However, it is widely observed that different types of feedstock, pyrolysis conditions, or modification steps may result in different physicochemical properties of biochar. Although biochar is widely used as an adsorbent for various pollutants, its surface area is relatively low without any modification process (Yaashikaa et al., 2020). Biochar inherently possesses some carbonyl and hydroxyl functional groups. However, the amount is minimal compared to its bulk surface. Physical and chemical modifications are often applied to enhance the performance of biochar.

Compared with physical modification, chemical modification is preferable as it directly influences the surface functionality of biochar (Tan et al., 2023a). It can be implemented at a lower temperature, produces a lesser amount of burn-off char and yields higher activity (Sajjadi et al., 2019). The chemical modification of biochar to

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enhance its functionality is an emerging field of study. It is the most crucial step to alter biochar's physical and chemical properties, such as surface area and surface functionality, to enhance the adsorption capacity of biochar for specific pollutants. Chemical modification facilitates the interactions of a modifying agent with the surface of biochar, thus providing substantial effects on the skeleton and biochar surface (Abegunde et al., 2020). It is a common method used to introduce the functional groups to the carbon surface of biochar, resulting in altered functional properties to overcome the limitations of untreated biochar for pollutant removal, soil remediation or wastewater treatment (Tan et al., 2021). For instance, the high adsorption capacity of chemically modified biochar towards various pollutants was associated with the increasing numbers of surface functional groups, surface area and porosity. The presence of functional groups on biochar will increase its hydrophilicity and subsequent interaction between the functional groups and adsorbate molecules, leading to higher efficiency in removing pollutants from soil or wastewater. The surface area and porosity increase the mobility of pollutants and facilitate their diffusion into biochar's internal structure (micropores). Abundant studies have reported that chemical modification has significantly improved the surface functionalities of biochar. However, limited work has extracted and analysed the effects of chemical modification on biochar physicochemical properties from different independent studies. Such information would guide the selection of suitable chemical modification methods to tailor biochar for different environmental applications. This review summarises the effects of chemical modification methods on the resultant physicochemical properties of biochar that can be used as an adsorbent for pollutant removal, soil amendment and wastewater treatment. In this study, different chemical modification methods, including (i) the activation using nitric acid (HNO_3), sulphuric acid (H_2SO_4), hydrochloric acid (HCl), phosphoric acid (H_3PO_4), sodium hydroxide (NaOH), potassium hydroxide (KOH), (ii) impregnation using magnesium oxide (MgO), calcium oxide (CaO), copper ($CuCl_2$), iron (III) chloride ($FeCl_3$), iron (III) sulphate (Fe_2SO_4) and (iii) magnetisation using iron (III) chloride ($FeCl_3$) and iron (II) oxide were explored. The potential applications of biochar are summarised.

2. Different chemical modification strategies for improving biochar adsorption performance

Various chemical modification strategies, including acid and base activation, nanomaterial impregnation and magnetisation, have been applied to improve the adsorption performance of biochar. Figure 1 shows the chemical modification methods, resultant biochar properties, and potential applications.

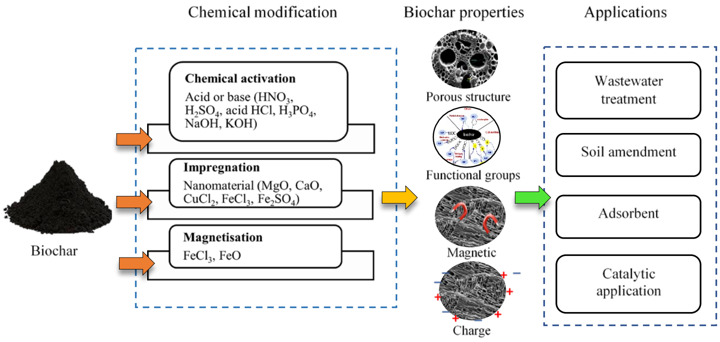

Figure 1: Na^+ Desorption efficiency of HNO3 EFB-BC with HCl as the desorption agent in six adsorption-desorption cycles

Chemical activation involves doping the biochar surface with a chemical reagent, widely used to modify the surface morphology and functionality of biochar. It can be done by soaking or suspending the pyrolysed biochar in the chemical reagent at a ratio of 1:10 (biochar: acid or base) under a specific reaction temperature (room temperature to 120 °C) and treatment time (Sajjadi et al., 2019). The secondary thermal treatment may be needed to enhance the effects of chemical activation to biochar with desired characteristics. Nanomaterial impregnation emerged as a new technology for producing biochar with specific selectivity and applicability towards targeted pollutants. It allows the uniform distribution of nanomaterial in the internal porous structure of biochar. Impregnation is performed through a method known as dip-coating. The biochar is immersed in a solution containing metal salts or metal oxides and stirred constantly for a specific duration, followed by filtering and drying (Sajjadi et al., 2019). In terms of magnetisation, it is a promising method to aid in separating biochar from the aqueous solution by using an external magnet. This contributes to the easy recovery of biochar after use. It usually involves fusing FeO or $FeCl_3$ into the carbon structure of biochar, forming ferromagnetic particles. The chemically modified biochar has demonstrated a great potential for wastewater treatment, soil amendment, pollutant removal and catalytic applications. Table 1 presents the chemical modifications method, pollutants removed by the chemically modified biochar as reported by previous studies, and biochar properties' physical and chemical changes.

Table 1: Effects of chemical modification on biochar and its applications

Methods	Reagent	Potential applications/ pollutant removal by previous studies	Physical/ chemical changes						Reference
			Increase surface area, porosity	Formation of new adsorption sites	Enhance oxygen-containing functional groups	Low pH_{pzc}	Increase polarity	Reduce ash content	
Activation	HNO_3	Methylene blue dye, iodine, carbon tetrachloride		✓	✓	✓	✓	✓	Babatunde et al. (2016) Peiris et al. (2019)
	H_2SO_4	Ammonium	✓		✓	✓	✓	✓	Wang et al. (2020) Peiris et al. (2019)
	HCl	Ammonium	✓		✓	✓	✓	✓	Wang et al. (2020) Peiris et al. (2019)
	H_3PO_4	Methylene blue dye, sulfadiazine, 2,4-dichlorophenol, copper and cadmium	✓		✓	✓	✓		Zeng et al. (2022)
	NaOH	Methylene blue and malachite green dye	✓						Liu et al. (2020) Mustapha et al. (2021)
	KOH	Sodium ions	✓					✓	Rostamian et al. (2015) Rostamian et al.(2018)
Impregnation	MgO	Carbon dioxide		✓					Shahkarami et al. (2016)
	CaO	Phosphate		✓					Dalahmeh et al. (2020)
	$CuCl_2$	Organic matter, phosphate		✓					Tomin et al. (2021)
	$FeCl_3$	Phosphate		✓					Tomin et al. (2021)
	$FeSO_4$	Methylene blue dye		✓					Tomin et al. (2021)
Magnetisation	$FeCl_3$	Mercury, heavy metals, nuclear waste pollutants, organic and inorganic anion pollutants, photocatalytic carrier		✓	✓				Yang et al. (2016) Zhao et al., (2021)
	FeO	Phosphate		✓					Chen et al. (2011)

Based on the data obtained, it can be seen that the acid activation involving HNO_3, HCl, H_2SO_4 and H_3PO_4 produces biochar with abundant oxygen-containing functional groups, lower pH_{pzc}, higher polarity and lower ash content. The use of different acidic reagents may lead to the development of different surface functional groups. Based on the previous research (Peiris et al., 2019), HNO_3 activation of biochar causes functional group fixation via nitration and oxidation, thus promoting the formation of -nitro (NO_2) and carboxylic acid (-COOH) functional groups. Upon H_3PO_4 activation, the biochar has developed new functional groups such as P=O and P=OOH that may interact with pollutants to form surface complexes (Zeng et al., 2022). HCl activation enhances the oxygen-containing functional groups by reducing carbonyl groups such as phenol, ethers and lactones (Peiris et al., 2019). These functional groups are mainly located on the edge of the basal plane or outer surface of biochar, enhancing biochar's hydrophilic and polar nature (Abegunde et al., 2020). The acid-activated biochar exhibited low pH_{pzc} and decreased ash content due to the demineralisation and introduction of acidic functionalities. With low pH_{pzc}, the negative charges dominate the surface of biochar, facilitating the adsorption of cationic pollutants through electrostatic interaction (Peiris et al., 2019).
Compared with HCl, H_2SO_4 and H_3PO_4 activated biochar, and the HNO_3 activation does not cause a significant change in surface area and porosity of biochar. At an early stage of HNO_3 activation, biochar's surface area and pore volume increased due to the formation of micropores and solubilisation of inorganic compounds or impurities in its structure (Sajjadi et al., 2019). The crystallites coagulated when activation proceeded, and the carbon layers broke up. There was an increase in the formation of oxygen-containing functional groups at walls and entrances of pores, thus narrowing the pore entrances (Sajjadi et al., 2019). The change in surface area and porosity of biochar becomes negligible. Among all acids, H_3PO_4 is a milder acid that can protect the carbon skeleton of biochar during the activation process. It also exhibits a greater advantage in micropore formation. Activation is a preferable strategy for altering the surface functionality of biochar, considering their environmental effects and less corrosive nature.
The alkaline activation can improve the number of alkali groups and non-polar surfaces, enhancing the adsorption capacity of biochar towards the pollutants. KOH and NaOH are two commonly used reagents for alkaline activation of biochar. Upon activation, the biochar exhibits mainly positive charges that can promote the adsorption of anionic pollutants. Based on Table 1, the NaOH and KOH activation has improved biochar's surface area and porosity. According to the previous studies (Rostamian et al., 2015), the KOH-activated biochar exhibits the highest surface area and pore volume than steam-activated biochar, contributing to the highest adsorption capacity (mg/g) towards sodium ions. However, some studies have reported the reduction of surface area and porosity of biochar after subjecting to alkali activation (Tan et al., 2017). This might be due to the usage of excess basic reagent or the prolonged exposure of biochar to high treatment temperatures. For instance, excess NaOH may result in a vigorous gasification reaction that destroys the carbon structure of biochar, rupturing the micropores and causing a significant reduction in accessible area (Sajjadi et al., 2019). Unlike acidic activation that will enhance the formation of oxygen-containing functional groups on the biochar surface, the alkaline activation by NaOH and KOH has reduced the number of functional groups. Initially, the KOH activation increased the number of surface functional groups, such as carboxylic, alcoholic, phenolic, aromatic, and alkenes groups. However, the surface oxygen groups on biochar decompose, and ash content decreases upon heating. The carbon content in KOH-activated biochar increased while the oxygen and hydrogen decreased remarkably due to the loss of volatile matter caused by the dehydration and elimination reactions (Kong et al., 2019). Similar findings were reported where the NaOH activation had reduced the oxygen-containing functional groups of biochar (Zheng et al., 2013).
Compared with KOH activation, there are fewer studies on NaOH chemical activation. NaOH activation is less corrosive, more environmentally, and cheaper as it requires a lower dosage (Hafizuddin et al., 2021). NaOH promotes a better chemical activation than KOH as the size of Na^+ is smaller than K^+ so that it can intercalate into the carbon structure of biochar easily (Kleber et al., 2015).
Impregnation involves loading the biochar with nanomaterial to enhance its catalytic or adsorption properties, offering tailored functionality. However, the process can be expensive due to the high cost of nanomaterials and the need for specialized equipment. Based on the results obtained, the main effect of impregnating biochar with MgO, CaO, $CuCl_2$, $FeCl_3$ and $FeSO_4$ was the formation of new active sites positively charged on the biochar surface, enhancing its capacity to adsorb anionic pollutants from soil or wastewater. For instance, by utilising $FeCl_3$ and CaO as the impregnation material, the biochar is enriched with Fe^{3+} and Ca^{2+}, resulting in effective phosphate adsorption through the formation of surface complexes and strong precipitates (Dalahmeh et al., 2020). Similar findings were reported where the adsorption capacity of Fe-impregnated biochar towards methylene blue dye is 95 % higher than the untreated biochar (Shah et al., 2015). Unlike acid or base activation, the impregnation of biochar with nanomaterial has decreased its surface area and porosity. This reduction indicates a successful impregnation of nanomaterial within the pores in the carbon structure of biochar. Previous research findings show a surface area of 571 m^2/g for pristine biochar (Tomin et al., 2021). Upon successful impregnation, the surface area of Cu^{2+} and Fe^{3+} impregnated biochar has reduced to 99 m^2/g and 92 m^2/g. They

further elaborated that biochar's high surface area and porosity play an important role during the nanomaterial impregnation process. The pores in the carbon structure act as hosts for the loading of nanomaterial. However, biochar's surface area and porosity might not play a major role compared to active sites during the adsorption of pollutants. This statement complements previous studies where Mg content increases from 3 to 10 wt. % has led to smaller surface area and higher removal of CO_2, suggesting that the nanomaterial content has a greater impact than porosity and surface area of biochar (Shahkarami et al., 2016).
Introducing a magnetic medium to biochar is an efficient method to separate the biochar efficiently by an external magnetic field. However, the drawback of biochar magnetisation is the reduction of BET surface area due to the formation of secondary iron hydroxide on the surface that has blocked the pores in biochar (Noraini et al., 2016). The magnetisation of biochar with $FeCl_3$ and FeO has reduced the surface area of biochar. However, the average pore radius of magnetic biochar was larger than the non-magnetic biochar. The magnetic biochar likely contains a considerable amount of iron oxide and iron chloride magnetite, resulting in a smaller surface area and abundant transitional pores (2-50 nm) (Chen et al., 2011). Combining different chemical modification strategies with magnetisation should be tested to obtain biochar with desired surface functionalities that can be recovered from the aqueous environment.

3. Conclusion

Biochar without chemical modification exhibits low surface area, porosity, functional groups and adsorption sites. Different innovation strategies have been applied to improve the physicochemical properties of biochar. This paper has reviewed different chemical modification methods, including the activation using acid or base, nanomaterial impregnation and magnetisation. Following acid activation (HNO_3, HCl, H_2SO_4 and H_3PO_4), the biochar has low pH_{pzc}, increased oxygen-containing functional groups, polarity and decreased ash content. HCl, H_2SO_4 and H_3PO_4 activated biochar possess high surface area and porosity, except HNO_3 activated biochar. Base activation using NaOH and KOH has increased the surface area, porosity, amount of alkali groups and non-polar surfaces, thus enhancing the adsorption capacity of biochar towards the pollutants. The impregnation of biochar with MgO, CaO, $CuCl_2$, FeO, $FeCl_3$ and $FeSO_4$ is considered a cationic modification that can enhance its selectivity and specificity toward anionic pollutants. The magnetisation of biochar with $FeCl_3$ and FeO donates the ferromagnetic properties to biochar. This enables the fast separation and easy recovery of magnetic biochar from an aqueous solution, making it an economically attractive alternative in the industry. Future research should focus on improving the efficiency of modification processes and chemical recovery to prevent chemical wastage and produce biochar with desired characteristics for industrial-scale application. The lifecycle assessment of modified biochar should be explored to comprehensively evaluate its environmental, economic, and social impacts from production to end-of-life, ensuring it aligns with sustainable development goals (SDGs)."

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