

# 改性生物炭吸附废水中重金属离子的研究进展

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**摘 要:** 随着现代工业的发展, 重金属水污染日益严重, 对水生生态环境和人类健康构成潜在威胁。生物炭作为一种高效、低成本的吸附剂, 对重金属离子有一定的吸附能力, 经过改性后其吸附能力显著增强, 合理利用生物炭能有效缓解环境污染问题。本文综述了生物炭的改性方法, 对比了物理改性、生物改性和化学改性等不同改性方法的优缺点, 分析了改性生物炭对重金属离子吸附能力的影响, 总结了生物炭的改性机理。在此基础上, 指出了未来生物炭在共存污染物问题的研究方向, 为生物炭在重金属废水净化领域的应用提供了重要参考。

**关键词:** 改性生物炭; 吸附; 废水; 重金属

## Research progress in the adsorption of heavy metal ions from wastewater by modified biochar

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**Abstract:** The rapid development of modern industries is accompanied with the aggravating

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water heavy metal pollution, which poses a potential threat to the aquatic environment and the health of local populations. As an efficient and economical adsorbent, biochar demonstrates the adsorption capacity for heavy metal ions and its adsorption capacity is significantly enhanced after modification. Therefore, biochar can effectively mitigate environmental pollution. By reviewing the existing studies, we summarize the modification methods of biochar, compare the advantages and disadvantages of physical, biological, and chemical modification methods, analyze the effects of modification on the adsorption capacity of biochar for heavy metal ions, and expound the modification mechanism of biochar. On this basis, this article puts forward the future research directions of the application of biochar in treating coexisting pollutants, aiming to provide a reference for the application of biochar in the purification of heavy metal-containing wastewater.

**Keywords:** modified biochar; adsorption; wastewater; heavy metals

随着采矿、冶炼、电镀、化工等工业的发展,重金属的扩散、沉降、积累使得土壤及水体中重金属污染问题日益严重,因此寻找高效、经济、环保的治理方法对缓解重金属污染具有重要意义。生物质具有成本低、来源广泛、绿色、循环再生、可生物降解等优点<sup>[1]</sup>,主要以作物秸秆和枯枝落叶等农林废弃物,动物粪便等畜牧养殖废弃物,市政污泥、木屑及甘蔗渣等工业生产废弃物,以及厨余垃圾和生活垃圾等生活废弃物的形式存在<sup>[2-3]</sup>。在缺氧或无氧条件下,通过热化学反应将上述生物质转化成具有较大比表面积和较丰富表面官能团的多孔、富碳材料,即生物炭<sup>[4]</sup>,将生物炭应用于吸附

水体中的铅、铬、汞、镉、铜、锌等重金属离子既是目前废水处理的研究热点,同时也实现了生物物质的高值化利用。

原生物炭孔隙结构及表面官能团数量具有局限性<sup>[5]</sup>,对废水中的重金属离子的吸附能力有限,研究表明可通过多种改性方法提高其吸附性能<sup>[6]</sup>。

基于此,本文在综合国内外研究的基础上,对生物炭的改性方法、不同改性方法的优缺点以及吸附机理进行了总结,探索了未来生物炭在处理含重金属离子废水以及共存污染物问题的研究方向及潜在应用,为生物炭在重金属污染的废水净化领域的应用提供了重要参考。生物炭的制备及改性摘要如图1所示。

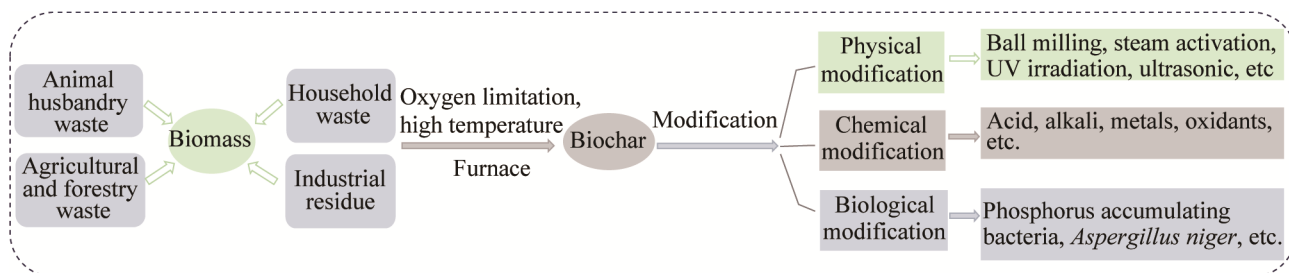


图1 生物炭的制备及改性摘要图

Figure 1 Summary diagram of preparation and modification of biochar.

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# 1 生物炭的改性方法

生物炭的改性是指通过物理和化学方法激活原始生物炭,以获得具有优异性能的生物炭的过程,其主要作用是生物炭的多孔结构增加比表面能、破坏其化学稳定性、导致更高的芳香结构和更少的极性官能团、并为重金属的吸附提供额外的有效位点<sup>[7]</sup>,从而提高生物炭对重金属离子的吸附能力。生物炭的改性方法主要有物理法、化学法和生物法。物理改性主要包括球磨改性、蒸汽改性、紫外线照射等;化学法主要包括酸碱改性、有机改性、金属改性等。生物炭改性形式主要有2种:一种是表面结构改性,通过改变生物炭孔隙结构,增加比表面积;另一种是表面化学改性,通过改变生物炭表面官能团,增加生物炭表面吸附位点<sup>[8]</sup>。

## 1.1 化学法

化学法主要是通过化学物质活化生物炭和在生物炭上负载化学物质来提高生物炭对重金属的吸附性能。因生物炭的种类和被吸附的重金属离子的不同,导致用来活化生物炭的化学物质种类繁多,常用的有酸、碱、磷酸盐以及氧化剂等。

### 1.1.1 酸碱改性

常用到的酸碱有盐酸、硫酸、硝酸、磷酸、草酸、柠檬酸、KOH、NaOH、 $\text{Na}_2\text{CO}_3$ 、 $\text{K}_2\text{CO}_3$ 等,Choudhary等<sup>[9]</sup>使用硫酸对棕榈空果串生物炭进行酸改性,显示生物炭的含碳量从65%增加到了78%,改性后的生物炭吸附能力更强、平衡速度更快,并且在多组分系统和实际废水中的除污率达到70%–75%;Xu等<sup>[10]</sup>通过 $\text{H}_3\text{PO}_4$ 对茶枝生物炭进行改性,发现 $\text{H}_3\text{PO}_4$ 能改变原始生物炭的理化性质,在相同条件下,改性后的生物炭对 $\text{Cd}^{2+}$ 和 $\text{Pb}^{2+}$ 的最大吸附量分别是原始生物炭的1.5倍和1.3倍。Zhao等<sup>[11]</sup>采用磷酸活化制备柚子皮改性生物炭用于吸附Ag(I)

和Pb(II)离子,经酸改性后的生物炭均显示更优异的吸附性能。经过碱改性的生物炭引入了更丰富的含氧官能团,增大了其孔隙率,Anthonyamy等<sup>[12]</sup>用KOH活化橡胶种子壳生物炭,发现生物炭对NO的吸附量从17.8 mg/g提升至63.0 mg/g;Wang等<sup>[13]</sup>在450 °C下将大豆秸秆或油菜秸秆制成生物炭(即soybean straw biochar, SBB或rape straw biochar, RSB),并用石灰 $\text{Ca}(\text{OH})_2$ 进行改性制备碱改性生物炭,得到Ca-SBB与Ca-RSB,发现Ca-SBB与Ca-RSB对 $\text{Cd}^{2+}$ 的最大吸附量分别是原始生物炭的1.56倍和1.48倍, $\text{Ca}(\text{OH})_2$ 的修饰有效地提高了离子交换作用,降低了官能团络合作用,导致改性后的生物炭对镉的吸附量提高。

酸碱改性是一种被广泛使用的改性方法,能使用的酸碱较多,操作简单且改性效果显著;酸碱改性可以在一定程度上改变生物炭C、H、O的含量以及改善生物炭孔隙结构,从而提高其吸附性能,但选择一种更加绿色环保的溶剂进行改性仍是未来探究的重点。

### 1.1.2 有机改性

有机改性是利用有机溶剂,如聚乙烯亚胺等醇类,草酸、柠檬酸等酸类,丰富其表面含氧官能团,从而增强生物炭的吸附能力。Tan等<sup>[14]</sup>利用壳聚糖对猕猴桃生物炭(kiwi biochar, KB)进行改性,得到一种新型壳聚糖改性猕猴桃枝生物炭(chitosan modified kiwi branch biochar, CHKB),结果表明,KB对Cr(II)的吸附量为4.26 mg/g,而CHKB对Cr(II)的吸附量为126.58 mg/g;壳聚糖增大了原始生物炭的比表面积,并且在其表面增加了-OH、-NH等官能团,提高了CHKB的吸附性能。

利用有机溶剂对生物炭进行改性可以丰富生物炭表面含氧官能团,增加更多活性位点。但有机溶剂易挥发等特性可能会在改性过程中

造成浪费,如果在改性过程中进行冷凝回收操作,将部分挥发的有机溶剂回收对生物炭进行二次改性,可能会进一步提高生物炭的吸附性能。

### 1.1.3 金属改性

通过负载功能化合物制备复合生物炭是提高生物炭对重金属离子吸附性能的重要途径。常用的负载物有单质金属及其氧化物,纳米尺度的金属及其氧化物能在生物炭表面提供更多吸附位点。纳米零价铁因其易获得性和高反应活性,被认为是修复各种污染物的强还原剂,Liu 等<sup>[15]</sup>在洋麻生物炭表面负载零价铁纳米粒子能显著提高对 Cu(II)离子的吸附。在金属及其氧化物基础上负载功能性的化合物能更有效地提高改性生物炭的吸附性能,吴卫蔚等<sup>[16]</sup>报道了以麦秆为原料,利用不同铁改性剂( $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ,  $\text{Fe}^0$ )制得 4 种磁性生物炭,用于 Cr(VI)离子吸附,研究表明,  $\text{Fe}^{2+}$ 能更有效地提高生物炭磁性,  $\text{Fe}^{3+}$ 和  $\text{Fe}^{2+}$ 参与改性均使得生物炭吸附性有所提升,而  $\text{Fe}^0$  改性使生物炭吸附性变弱,  $\text{Fe}^{3+}/\text{Fe}^{2+}$ 共同改性的生物炭吸附性最佳;  $\text{Fe}^{3+}/\text{Fe}^{2+}$ 改性生物炭比表面积达  $33.73 \text{ m}^2/\text{g}$ ,对 Cr(VI)的去除率达 95.77%。金属改性通过将金属离子引入生物炭,提高生物炭磁性,并在生物炭上增加更多的吸附位点,从而提高原生生物炭的吸附性能。

当在生物炭表面负载金属或金属氧化物后,负载的金属或氧化物可以作为生物炭表面新增加的活性位点,提供更多吸附位点,并且经过金属改性后生物炭的得率会有所提高。

### 1.1.4 氧化剂改性

氧化剂改性是一种较为常见的化学改性方式,常用的氧化剂有过氧化氢、高锰酸钾、具氧化性的酸碱等。Kushwaha 等<sup>[17]</sup>利用高锰酸钾改性花生壳生物炭,改性后的花生壳生物炭比表面积增加且孔体积也有所增大,其表面特性

得到改善,为生物炭提供了更多的吸附位点,从而增大吸附容量;Zuo 等<sup>[18]</sup>用不同浓度的  $\text{H}_2\text{O}_2$  对生物炭进行改性,发现经 20%  $\text{H}_2\text{O}_2$  改性的生物炭对 Cu(II)的吸附量最大,原因是通过 20%  $\text{H}_2\text{O}_2$  改性的生物炭表面附有大量羧基,而羧基主要负责对 Cu(II)的吸附。

氧化剂改性生物炭能增大生物炭比表面积,扩大生物炭孔体积,氧化剂的加入可以丰富生物炭表面官能团,并且添加氧化剂可以通过氧化还原反应对重金属进行吸附。但经过氧化剂改性过的生物炭吸附重金属能力受到 pH 的影响较大,吸附不同重金属时 pH 也不同。图 2 为不同化学法改性后生物炭的差异。

## 1.2 物理法和生物法

### 1.2.1 物理法改性

常用的物理方法有球磨处理、蒸汽活化和紫外辐照等。球磨处理主要通过球介质的高速运动,将生物炭磨成纳米尺寸,增加生物炭比表面积,暴露表面官能团,从而提高其吸附能力;Wang 等<sup>[19]</sup>研究了球磨辅助处理对辛烯基琥珀酸酐(octenyl succinic anhydride, OSA)改性青稞淀粉(highland barley starch, HBS)的取代度以及对 HBS 理化性质和结构的影响;结果表明,随着球磨时间的增加和球磨助剂的时间延长,

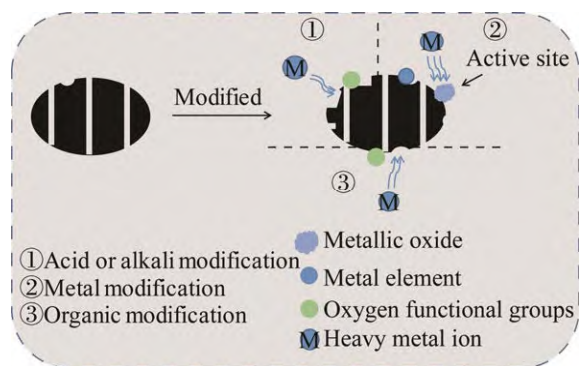


图 2 不同化学改性生物炭对比图

Figure 2 Comparison of different chemical modification of biochar.

OSA 改性的 HBS 表面形态越来越粗糙, 颗粒形态和晶体结构受到破坏; OSA 改性的 HBS 的短程有序性显著降低的时间也延长, 相对结晶度下降, 热稳定性下降。蒸气活化主要通过挥发生物炭内的成分, 增大其表面积及孔隙大小, 从而增强吸附能力。Wang 等<sup>[20]</sup>采用蒸汽活化对竹炭生物炭改性, 发现改性后生物炭对 Cu(II) 离子的吸附性能有明显提高。经过紫外辐照的生物炭具有更大的比表面积, 表面有更加丰富的含氧官能团。Peng 等<sup>[21]</sup>通过紫外光照射对玉米秸秆生物炭进行改性, 改性后的生物炭对 Cr(VI) 的吸附量为 20.04 mg/g, 而原始生物炭对 Cr(VI) 的吸附量仅为 1.11 mg/g, 提高了 18.1 倍。

物理改性使生物炭比表面积增加,孔隙结构丰富度也有一定改善,但相较于化学改性,经过

物理改性后的生物炭吸附性能提高并不显著。

### 1.2.2 生物法改性

生物法是通过微生物处理生物炭增大生物炭比表面积、增大孔隙容量，从而提高其吸附性能，Yang 等<sup>[22]</sup>考察了负载枯草芽孢杆菌的玉米芯生物炭(corn cob biochar loaded with *Bacillus subtilis*, CB@B)对镉的固定化效率和性能；在不同的热解温度下产生的 CB@B 均获得了优越的孔结构和丰富的 O-官能团(C=O、COOH、OH 和 Si-O-Si)，在溶液中进行吸附实验，显示 400 °C 下 CB@B 使 Cd(II)浓度降低了 81.21%，而未负载枯草芽孢杆菌的玉米芯生物炭仅使 Cd(II)浓度降低 5.70%，可见负载枯草芽孢杆菌的生物炭吸附效果明显。表 1 列举了部分生物炭改性方法及改性原理。

表 1 生物炭改性方法及改性原理

Table 1 The methods and mechanisms of biochar modification

| Modification methods |                                       | Modification mechanisms                                                                                                                                                                                | References |
|----------------------|---------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| Physical methods     | Ball milling modification             | Grinding solid particles to the nanoscale and increasing specific surface area by ball milling medium                                                                                                  | [23-24]    |
|                      | Steam activation modification         | Selective removal of volatile substances formed within the original biochar structure by water vapor, CO <sub>2</sub> , etc. to increase surface area with temperature rising and reduce pore diameter | [25-26]    |
|                      | UV irradiation modification           | Enhancement of the functional groups on the surface of biochar to improve its adsorption performance by UV irradiation                                                                                 | [27]       |
|                      | Ultrasonic modification               | Enlargement of the specific surface area and increasing the number of pores of biochar after ultrasonic modification                                                                                   | [28]       |
|                      | Microwave modification                | Changed the pore structure of biochar and provided more adsorption sites after microwave modification                                                                                                  | [29]       |
| Chemical methods     | Acids and alkalis modification        | By increasing the surface acid-base functional groups of biochar to increase the porosity, and improve the adsorption performance of biochar                                                           | [30-31]    |
|                      | Organic solvents modification         | By using organic solvents to increase the oxygen-containing functional groups on the surface of the original biochar and enhance its adsorption performance                                            | [32-33]    |
|                      | Metal modification                    | Provide more active sites for biochar and increase its magnetism to enhance its adsorption performance by combining metal oxides or elemental substances with the original biochar                     | [34-35]    |
| Biological method    | <i>Bacillus subtilis</i> modification | Increase its specific surface area and pore capacity and improve its adsorption performance after microbial treatment of biochar                                                                       | [36]       |

### 1.3 改性方法的联用

对生物炭进行多种改性方法联用能显著提高重金属吸附能力。Wang 等<sup>[37]</sup>对生物炭进行过氧化氢和硝酸活化，然后负载纳米零价铁，显著提高生物炭对 As(V)和 Ag(I)离子的吸附能力。Sajjadi 等<sup>[38]</sup>采用物理化学联用法处理松木生物炭，首先用超声处理，然后用磷酸活化，最后用二乙醇胺(diethanolamine, DEA)胺化，Ni(II)离子的去除率达到 71%。

联合改性是目前对生物炭改性的探究重点，通过将物理法、化学法、生物法结合对生物炭进一步改性，得到石墨化程度更高、吸附性能更加优异的生物炭。但联合改性对生物炭吸附性能的影响及机制了解还不够全面，需要进一步研究。

根据生物炭材料不同、废水中重金属离子的种类不同，宜采用不同的改性方法，不同改性方法也有各自的优势和不足，表 2 总结了 3 种改性方法的优缺点。

## 2 改性生物炭对吸附重金属离子能力的影响

生物炭改性通过改善生物炭的表面结构，

增强其对重金属离子的物理吸附作用；或者通过改性引入特定的基团，改变生物炭的表面化学性质，促进其与重金属离子发生化学吸附，以达到去除重金属离子的目的。研究表明，有诸多因素会影响生物炭的改性，例如生物炭原材料的制备方法<sup>[47]</sup>、改性方法以及吸附条件等<sup>[48]</sup>。通过对比在不同因素下生物炭改性效果差异性，揭示生物炭在改性过程中的作用机理，在实际设计和开发中，可针对不同生物炭原料和重金属离子污染物选择合适的改性方法。

本文总结了原生物炭与改性生物炭对重金属离子吸附量的变化，在表 3 中列举了不同改性方法、不同生物炭原料以及不同重金属离子污染物对生物炭吸附能力的影响。例如：张越等<sup>[57]</sup>以氨气、硝酸、硫化钠和溴水 4 种化学试剂分别对松木屑生物炭进行表面改性，结果表明氨气改性生物炭对 Cd(II)离子的吸附效果最优。杨帆等<sup>[49]</sup>分别以苹果枝和葡萄枝为原材料的 2 种生物炭进行四乙烯五胺改性，吸附溶液中的 Zn(II)离子，发现 2 种改性生物炭对 Zn(II)离子的饱和吸附量分别为 52.9 mg/g 和 46.3 mg/g，远远大于原材料未改性的生物炭对 Zn(II)离子的饱和吸附量(21.7 mg/g, 33.0 mg/g)，饱和吸附量分别增大 143.8%和 40.3%，吸附量的差异是由于

表 2 三种生物炭改性方法优缺点

Table 2 Advantages and disadvantages of three biochar modification methods

| Modification methods    | Advantages                                                                                                                           | Disadvantages                                                                                                                                                                                                                                    | References           |
|-------------------------|--------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------|
| Physical modification   | Simple and easy to operate, environmentally friendly                                                                                 | High cost and unsuitable for large-scale industrial applications                                                                                                                                                                                 | [39-42]              |
| Chemical modification   | A significant effect on the physical and chemical properties of carbon materials, such as specific surface area and adsorption sites | Acids and alkalis are corrosive and not environmentally friendly enough<br>Further harmless treatment required, high costs<br>The adsorption effect is greatly affected by the environmental pH value, and the adsorbent is difficult to recover | [43]<br>[44]<br>[45] |
| Biological modification | Economical and environmentally friendly, reducing the use of toxic and harmful chemicals                                             | High cost, slow speed, bad stability, and poor reusability                                                                                                                                                                                       | [46]                 |

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表 3 改性生物炭对重金属离子吸附量影响  
Table 3 Influence of biochar modification on adsorption capacity of heavy metal ions

| Samples       | Modification methods                                                            | Factors of adsorption                                                                                      | Adsorbed ions          | Adsorption capacity or removal rate | References |
|---------------|---------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------|------------------------|-------------------------------------|------------|
| Apple branch  | Modification by tetraethylenepentamine                                          | Time, initial concentration and pH value                                                                   | Zn(II)                 | 13.2→52.2 mg/g                      | [49]       |
| Vine branch   | Modification by tetraethylenepentamine                                          | Time, initial concentration and pH value                                                                   | Zn(II)                 | 24.6→45.9 mg/g                      | [49]       |
| Rice straw    | Modification by a mixture of H <sub>2</sub> O <sub>2</sub> and HNO <sub>3</sub> | Contact time, initial pH value and initial concentration                                                   | Cd(II)                 | 69.3→93.3 mg/g                      | [50]       |
| Rice straw    | Modification by KOH solution                                                    | Cd ion concentration, the pH of Cd(II) Cd solutions                                                        |                        | 12.1→41.9 mg/g                      | [51]       |
| Rice straw    | Loaded by hydroxyapatite                                                        | Initial pH, contact time, initial heavy metal ion concentrations, NaCl concentration and competing cations | Pb(II), Cu(II), Zn(II) | 561.8→1 000.0 mg/g                  | [52]       |
| Rice straw    | Fabricated by iron floc generated from acid mine drainage (AMD)                 | pH value                                                                                                   | Pb(II)                 | 34.3→247.3 mg/g                     | [53]       |
| Coconut shell | Modification by KMnO <sub>4</sub>                                               | Initial pH, biochar dosage                                                                                 | Cd(II), Ni(II)         | 57.2 mg/g, 23.3 mg/g                | [54]       |
| Corn straw    | Loaded by <i>Bacillus subtilis</i>                                              | pH value                                                                                                   | Cd(II)                 | 62.0%                               | [55]       |
| Corn straw    | Modified by Fe-Mn                                                               | pH, high concentrations of humic acid                                                                      | Cu(II), Cd(II)         | 64.9 mg/g, 101.0 mg/g               | [56]       |

“→” indicates adsorption capacity of biochar for heavy metal ions before and after modification.

不同生物质原料制备生物炭，导致生物炭表面基团不同所造成的。在一定条件下采用不同改性方法，改性生物炭的吸附能力变化有明显差异。

然而，也有研究表明生物炭改性后没有明显的吸附效果。如 Shim 等<sup>[58]</sup>利用蒸汽活化芒草生物炭，改性后生物炭相较于原生物炭对 Cu(II) 离子的吸附能力没有明显差异，初步分析是由于蒸汽活化使生物炭表面积增加了近 1 倍，同时通过官能团的降解使其极性降低，导致和原生物炭具有相似的铜吸附能力。可见，针对不同原材料选择合适的改性方法及其相应的改性机理仍需做进一步的探索。

3 生物炭改性机理

由于生物炭具有丰富的表面基团和较大的

比表面积，因此能够吸附水溶液中的重金属离子。在生物炭的制备过程中，表面会残留一定的热解产物，导致生物炭的比表面积较小和表面的吸附位点较少，因此需要对生物炭进行改性以提高其对重金属离子的吸附能力。Chen 等<sup>[59]</sup>报道了负载 Fe<sub>3</sub>O<sub>4</sub> 纳米颗粒的蟹壳生物炭吸附 As(III)和 Pb(II)双金属离子体系，通过静电相互作用和形成 Pb-As(III)-Fe<sub>3</sub>O<sub>4</sub> 三元表面络合物提高对重金属离子的吸附能力。Peng 等<sup>[60]</sup>使用海藻酸钠和沸石咪唑酸盐对玉米芯生物炭进行改性吸附 Pb<sup>2+</sup>，发现改性后的生物炭比表面积有较大的提高，并且在吸附 Pb<sup>2+</sup>过程中，羧基与羟基起主要作用。目前生物炭的改性研究主要致力于增大生物炭的比表面积和微孔结构、增加生物炭表面吸附位点来提高其对重金属离子的吸附能力。

### 3.1 生物炭表面结构改性

生物炭的表面结构改性主要体现在增大比表面积和改变孔隙结构,这种表面结构的改性使生物炭有结合重金属离子的强烈倾向,从而能够较好地去除溶液中的重金属离子。Kim 等<sup>[61]</sup>在生物质热解过程中使用  $\text{CO}_2$  作为反应气体介质,对不同类型的生物质进行吹扫  $\text{CO}_2$  改性,可以增加生物炭的比表面积和孔隙总体积,从而增强吸附能力。生物炭的表面结构改性机理如图 3 所示。

### 3.2 生物炭表面化学改性

生物炭的表面化学改性主要集中在表面官能团的改变和化学吸附位的增加,化学吸附的作用有静电作用、离子交换作用和表面络合或沉淀作用。通过化学改性后的生物炭表面会与一些有害离子(As、Cr 等)之间通过正负电荷相互吸引或排斥产生作用;也可以从溶液中提取重金属离子(Cd、Pb 等)进行可逆等价交换反应,属于传质分离过程;或者改性后的生物炭表面分子或离子与重金属离子(Hg 等)相互结合形成非常稳定的新离子或沉淀物,化学吸附的机理如图 4 所示。

增加生物炭表面化学吸附位主要通过以下 4 种改性方法:(1) 引入功能官能团,一般有含氧官能团、氨基官能团。Hadjittofi 等<sup>[62]</sup>研究了

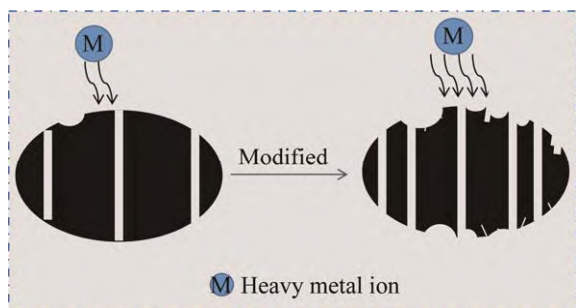


图 3 生物炭改性增强表面物理吸附能力机理图  
Figure 3 Inferred mechanism diagram of surface physical adsorption capacity enhanced by biochar modification.

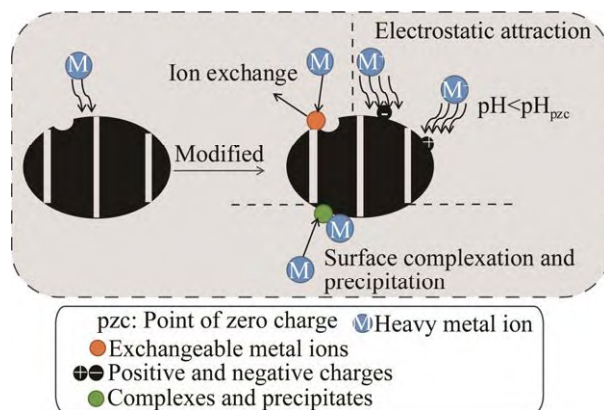


图 4 生物炭改性增加表面化学吸附位点机理推断图  
Figure 4 Inferred mechanism diagram of surface chemisorption sites added by biochar modification.

Figure 4 Inferred mechanism diagram of surface chemisorption sites added by biochar modification.

$\text{HNO}_3$  改性仙人掌生物炭对  $\text{Cu(II)}$  的吸附,通过 FT-IR 发现  $\text{HNO}_3$  改性之后出现了羧基官能团,表现出对  $\text{Cu(II)}$  离子较高的容量和化学亲和力。Zhang 等<sup>[63]</sup>将氨基引入稻草秸秆生物炭,改性生物炭( $\text{BC-NH}_2$ )的吸附能力提高了 72.1%。Liu 等<sup>[64]</sup>采用硫脲改性猪场污泥生物炭,引入表面官能团如  $\text{C-O}$ 、 $\text{C=O}$  以及  $\text{C=S}$ 、 $\text{C-S}$  和  $\text{RSO}_3^-$ ,可以通过配位和离子交换吸附  $\text{Pb(II)}$ 。(2) 引入具有离子交换能力的化学物质。Zhang 等<sup>[65]</sup>采用氯化镁改性小龙虾壳生物炭吸附  $\text{Pb(II)}$  离子,  $\text{Pb(II)}$  与  $\text{Mg(II)}$  离子交换能力优于  $\text{Pb(II)}$  离子与原生物炭表面的  $\text{Ca(II)}$  离子,增强了离子交换能力,从而提高了生物炭对  $\text{Pb(II)}$  离子的吸附能力。Zuo 等<sup>[66]</sup>研究了  $\text{CaCO}_3$  纳米颗粒改性的污泥生物炭对水中  $\text{Cd(II)}$  离子的去除,结果表明,镉(II)离子在改性生物炭上的吸附机制涉及重金属离子与  $\text{CaCO}_3$  纳米颗粒和生物炭之间的离子交换。(3) 引入络合物或沉淀物,使重金属离子在生物炭表面形成络合物或沉淀物。Tan 等<sup>[67]</sup>研究了锰如何对玉米秸秆生物炭进行改性,在生物炭表面  $\text{Cd(II)}$  离子和  $\delta\text{-MnO}_2$  之间形成络合物,提高了  $\text{Cd(II)}$  离子的去除率。(4) 引入磁性

粒子。Ifthikar 等<sup>[68]</sup>加入氯化铁制备的多孔污泥生物炭含有丰富的活性位点和磁性,与 Pb(II)离子之间存在静电吸引、络合和共沉淀等多重作用力,从而提高生物炭对 Pb(II)离子的去除效率。

## 4 结语

生物炭作为一种低成本材料,对重金属离子具有较好的吸附效果,被广泛应用于污水处理,提高生物炭对重金属离子的吸附能力一直是研究的重点。虽然改性生物炭作为吸附剂处理污水取得了不少研究成果,但仍需从以下方向进行更加深入的研究:(1) 生物炭作为吸附剂,其吸附效果除了受生物炭原材料、制备条件(如温度、速率、浓度和化合物的选择、固溶比等)和吸附条件(如温度、pH 等)影响外,还需研究共存离子对污染物吸附效果的影响;(2) 目前改性方法比较单一,吸附效果不够理想,可探讨多种改性方法的组合在污水处理中的应用;(3) 如今制备的改性生物炭只针对单一物质的吸附,但实际废水中成分复杂,含有多种重金属离子和有机物等共存污染物,需进一步研究生物炭对复杂体系的吸附能力,以及在控制改性生物炭制备成本下如何改善现有技术等;(4) 改性生物炭被利用后,应该如何回收才能保证不会对环境造成负担,或者如何使改性生物炭具有重复利用性,都值得进一步探索。

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