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生物炭-壳聚糖磁性复合吸附剂的制备及去除地下水中铅和铜

杨梦楠¹, 孙晗¹, 曹海龙¹, 贾增华¹, 冯政远², 郑丽君², 陈男^{2*}

(1. 国土环境整治中心, 中国地质工程集团有限公司, 北京 100093;

2. 中国地质大学(北京)水资源与环境学院, 地下水循环与环境演化教育部重点实验室, 北京 100083)

摘要: 壳聚糖作为天然多糖有机物, 具有对环境友好的特性, 其含有的大量含氮官能团可吸附水中的金属离子。但壳聚糖类吸附剂在酸性条件下适应性差, 实际使用过程中需要调节 pH 值, 因此增加了运行成本。本文选用农林废弃物花生壳(CC)和玉米芯(PS)制备生物炭, 与壳聚糖进行结合, 并引入磁性因子 Fe₃O₄, 制备了花生壳生物炭-壳聚糖磁性复合吸附剂(PSC)和玉米芯生物炭-壳聚糖磁性复合吸附剂(CCC), 并研究这两种吸附剂对水中 Pb²⁺和 Cu²⁺的吸附性能, 同时利用实际含多种金属离子的地下水对所制备的材料进行实验, 以评估其实际应用潜能。比表面积仪(BET)分析表征显示, CCC 相比 PSC 的比表面积和平均孔径更大, 两种吸附剂在 pH 4~7 范围内均表现出稳定的吸附性能。循环 5 个周期后, 两种吸附剂仍对 Pb²⁺和 Cu²⁺的去除率保持在 85% 以上, 表现出良好的循环利用性能。CCC 对 Pb²⁺和 Cu²⁺的最大吸附容量分别为 169.10mg/g 和 18.69mg/g, 均大于 PSC 的最大吸附容量。同时, CCC 可有效去除含重金属地下水中的多种金属离子。在处理实际含 Pb²⁺和 Cu²⁺的废水时可优先选择 CCC 材料作为吸附剂。吸附动力学实验结果表明, 两种材料对 Pb²⁺的吸附以物理吸附为主, 对 Cu²⁺的吸附以化学吸附为主。pH 值影响实验和 X 射线光电子能谱(XPS)表征结果说明两种材料主要通过静电吸引和含氮官能团与金属离子的螯合作用去除 Pb²⁺和 Cu²⁺。本文使用农林废弃物制备生物炭降低了成本, 引入的磁性因子方便了脱附过程, 生物炭-壳聚糖磁性复合材料的制备方法有效地改善了壳聚糖类材料在酸性条件下的适应性, 所制备的材料是一种去除地下水中 Pb²⁺和 Cu²⁺污染的有效潜在吸附剂。

关键词: 生物炭; 壳聚糖; 吸附; 铅; 铜; 含氮官能团; X 射线光电子能谱

要点:

- (1) 花生壳/玉米芯生物炭与壳聚糖的结合提高了壳聚糖类材料对不同 pH 值条件的适应性。
- (2) 生物炭-壳聚糖磁性复合材料主要通过静电引力和含氮官能团的螯合作用去除重金属。
- (3) 生物炭-壳聚糖磁性复合材料可有效地去除实际地下水中的 Cu²⁺、Pb²⁺、Cd²⁺和 Fe³⁺。

中图分类号: X523; G264.3

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由于采矿、选矿、冶炼、锻造、加工、运输等行业产生的含重金属废水的不恰当处置, 导致部分重金属特别是 Pb²⁺和 Cu²⁺进入地下水环境中, 污染地

下水^[1]。重金属可在人体内富集并参与生物循环, 在人体中长期积累会对人体带来致癌、致畸、致突变的风险, 尤其是对神经和肠胃系统^[2-3]。受污染的地下

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第一作者: 杨梦楠, 硕士研究生, 主要从事生态环境系统修复研究工作。E-mail: yangyangwd@hotmail.com。

通信作者: 陈男, 教授, 博士生导师, 地下水科学与工程专业, 主要从事地下水污染控制与修复技术研究。

E-mail: chennan@cugb.edu.cn。

水具有隐蔽性强和成分复杂等特点,处理难度较大,且各种不同化学形态的重金属离子无法通过水体的自净作用被去除^[4]。因此,为了保护生态系统的良性循环和人体健康,开发净化受重金属污染地下水的方法或材料是非常有必要的。目前常见的重金属去除方法主要有生物法^[5]、化学沉淀法^[6]、膜分离法^[7]和吸附法^[8]等。生物法处理重金属具有一定的局限性,因为微生物生长所需的环境条件比较苛刻,且产生的含重金属剩余污泥容易造成二次污染^[9]。化学沉淀法具有去除效率高的特点,但是大量混凝剂的使用导致了较高的处理成本^[10]。尽管膜分离法的去除效率较高,但是昂贵的膜片以及频繁的膜污染问题致使其不适用于处理重金属污染水体^[11]。吸附法由于其运营维护成本低、工程操作简单和不易产生二次污染等优点,在处理含重金属污染地下水方面受到广泛关注^[12]。

壳聚糖是自然界中存在的氨基碱性高分子多糖有机物,它的分子链上含有大量的官能团,如羟基基团($-\text{OH}$)和氨基基团($-\text{NH}_2$)。它们可以与重金属产生良好的螯合作用,且壳聚糖的来源广、成本低、可生物降解^[13]。但是,一般含重金属水体的pH为酸性,而壳聚糖在酸性条件下存在不稳定和易溶解的问题^[14]。因此,通过对壳聚糖的结构进行改性以解决上述问题,在壳聚糖分子链上引入其他功能基团是一种有效的方法。在众多功能基团中,吡咯基具有含氮杂原子的芳香性共轭环,例如2-吡咯甲醛,具有较强的供电子性和配位能力,若将它们引入到壳聚糖分子链上,可提高壳聚糖在酸性条件下的稳定性^[13]。生物炭是生物质在限氧或无氧条件下高温热解形成的富碳、高度芳香化、难溶性固态物质^[14]。与传统活性炭相比,生物炭含有丰富的官能团,表现出对重金属良好的吸附性能,且其原材料来源广泛、制备成本更低,因此学者们对生物炭净化含重金属水体方面进行了大量研究^[15-17]。但是原始生物炭存在粒径小、回收难的问题,这不利于生物炭在水处理领域的应用^[18-19]。

本研究使用花生壳和玉米芯制备了两种不同的生物炭,以2-吡咯甲醛作为壳聚糖的改性剂,添加 Fe_3O_4 赋予其磁性以提升材料的操作便利性。实验中联合使用生物炭、2-吡咯甲醛、壳聚糖和 Fe_3O_4 四种材料制备了生物炭-壳聚糖磁性复合吸附剂并用于 Pb^{2+} 和 Cu^{2+} 的吸附研究。利用扫描电子显微镜(SEM)、比表面积分析仪(BET)和X射线衍射仪(XRD)研究了吸附剂的物理化学性质;利用批试验

和数学理论模型研究了材料对 Pb^{2+} 和 Cu^{2+} 的吸附性能和理论吸附容量;使用实际地下水评估材料的实际应用潜能;使用X射线光电子能谱仪(XPS)对吸附前后材料的含氮官能团进行表征,分析参与吸附过程的官能团的种类以确定吸附机理。

1 实验部分

1.1 实验材料

花生壳和玉米芯的产地为江苏省连云港市东海县白塔埠镇。硝酸铅和硝酸铜用于配制铜和铅溶液。壳聚糖、冰乙酸、四氧化三铁和2-吡咯甲醛用于磁性壳聚糖的制备。盐酸和氢氧化钠用于调节溶液pH。乙二胺四乙酸二钠(EDTA-2Na)用于材料解吸。实验所需化学试剂均为分析纯,均购自国药集团化学试剂有限公司。

酸性矿山地下水取自安徽省大矾山东山区某矿区,所取地下水样品含As、Ca、Cd、Cu、Fe、Mn、Na和Ni金属离子,其含量分别为18.200 $\mu\text{g/L}$ 、40.541 mg/L 、3.800 $\mu\text{g/L}$ 、13.300 mg/L 、215.00 mg/L 、510.00 $\mu\text{g/L}$ 、81.694 mg/L 和87.000 $\mu\text{g/L}$,吸附前使用0.45 μm 的滤膜去除水中的杂质。

1.2 生物炭-壳聚糖磁性复合吸附剂的制备

称取一定量预处理后的生物质原料(花生壳和玉米芯),包裹三层铝箔纸使其置于限氧条件下,将其放于马弗炉中,以10 $^{\circ}\text{C}/\text{min}$ 速率升温,升至设定温度600 $^{\circ}\text{C}$,保持2h热解条件,之后将得到的生物炭粉未经室温冷却后过100目筛,保存备用。其中花生壳生物炭记作PS,玉米芯生物炭记作CC。

然后,称取10g壳聚糖置于1L烧杯中,将500mL浓度为5.0%的冰乙酸溶液倒入烧杯中,再将烧杯置于水浴锅中,在30 $^{\circ}\text{C}$ 条件下使用搅拌器机械搅拌1h,之后加入10g的2-吡咯甲醛,将水浴锅温度调至70 $^{\circ}\text{C}$,机械搅拌7h,再称取12g生物炭加入其中,在25 $^{\circ}\text{C}$ 条件下均匀搅拌1h后,加入10g的 Fe_3O_4 ,在温度不变的条件下机械搅拌1h,形成均匀黑色凝胶溶液。最后使用注射器将上述黑色凝胶溶液滴入1mol/L氢氧化钠溶液中,形成凝胶小球。使用去离子水反复清洗凝胶小球10次后,放入烘箱,在60 $^{\circ}\text{C}$ 条件下烘干24h,密封保存备用。花生壳生物炭-壳聚糖复合材料记作PSC,玉米芯生物炭-壳聚糖复合材料记作CCC。

两种材料合成的简易示意图见图1。

1.3 材料表征

采用扫描电镜(SEM, JSM-7610F, Quantachrome



图1 生物炭-壳聚糖磁性复合材料合成示意图

Fig. 1 Schematic diagram of biochar-chitosan magnetic composite.

公司)分析材料的微观形貌,在拍照记录前对材料样品进行喷金处理。材料的比表面积和孔隙体积使用比表面积分析仪(BET, iCAP 7300, Quantachrome 公司)进行测定,利用氮气在 -196°C 下对材料进行吸附-解吸测试。X射线衍射(XRD, D8 advance, Bruker 公司)用于分析材料表面晶体结构,使用 $\text{Cu K}\alpha$ 放射源在 $10^{\circ}\sim 80^{\circ}(2\theta)$ 范围内进行扫描。利用 X 射线光电子能谱仪(XPS, ESCALABXi+x, ThermoFisher 公司)分析材料表面官能团结构,采用单色 $\text{Al-K}\alpha$ 进行辐射(225W, 15mA, 15kV)。采用电感耦合等离子体发射光谱仪(ICP-OES, iCAP 7300, ThermoFisher 公司)测试溶液中的金属离子含量。

1.4 吸附实验

吸附实验在 50mL 锥形瓶和恒温摇床中进行,振荡频率为 150r/min,反应时间为 12h,反应结束后测定溶液中 Pb^{2+} 和 Cu^{2+} 的浓度。每组实验设置 2 个平行样。利用不同初始 pH 实验评价材料在不同 pH 条件下的吸附性能,利用动力学和等温线模型评价材料的吸附动力学过程和预测材料最大吸附容量,利用循环吸附实验和实际矿山地下水对材料的实际应用潜能进行评价。

1.4.1 初始 pH 的影响

初始 pH 的影响实验:分别称取 0.2g 吸附剂置于 6 个 50mL 锥形瓶中,采用盐酸和氢氧化钠调节溶液的 pH 值为 2.0、3.0、4.0、5.0、6.0 和 7.0,之后将调整好 pH 值的 50mg/L 的 $\text{Pb}^{2+}/\text{Cu}^{2+}$ 污染液置于锥形瓶内进行实验。

1.4.2 吸附动力学和吸附等温线实验

吸附动力学实验条件:称取 1.0g 吸附剂置于 250mL 锥形瓶中,加入 250mL 初始浓度为 50mg/L 的 $\text{Pb}^{2+}/\text{Cu}^{2+}$ 污染液,分别在 3、5、10、15、30、60、

180、300、420、720 和 1440min 时取样。

吸附等温线实验条件:分别称取 0.2g 吸附剂置于 9 个 50mL 锥形瓶中,加入 50mL 初始浓度分别为 1、10、25、50、100、200、300、400 和 500mg/L 的 $\text{Pb}^{2+}/\text{Cu}^{2+}$ 溶液。

1.4.3 材料循环利用和实际地下水验证评价实验

循环利用实验:使用 EDTA-2Na 作为脱附剂进行循环利用实验。将吸附后的材料置于浓度为 0.01mol/L 的 EDTA-2Na 溶液中,并调节溶液 pH 为 5.0,在 30°C 条件下振荡 30min,然后用去离子水进行清洗烘干后再次进行吸附实验,重复 5 个周期。

利用实际地下水对 CCC 材料的吸附性能进行评价:将 0.3g 的 CCC 和 50mL 实际地下水置于 50mL 锥形瓶中进行实验。

1.5 批实验数据分析方法

去除率和吸附量的计算采用以下公式(1)和(2)^[20-21]:

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

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

式中: η 代表去除率(%); C_0 代表溶液中 Pb^{2+} 和 Cu^{2+} 的初始浓度(mg/L); C_e 代表吸附平衡时溶液中 Pb^{2+} 和 Cu^{2+} 的浓度(mg/L); q_e 代表平衡时材料的吸附量(mg/g); V 代表溶液的体积(L); m 代表吸附剂的质量(g)。

2 结果与讨论

2.1 材料的表征

2.1.1 SEM 和 BET 表征

图 2 中 a 和 b 分别是 PS 和 CC 的 SEM 图像。

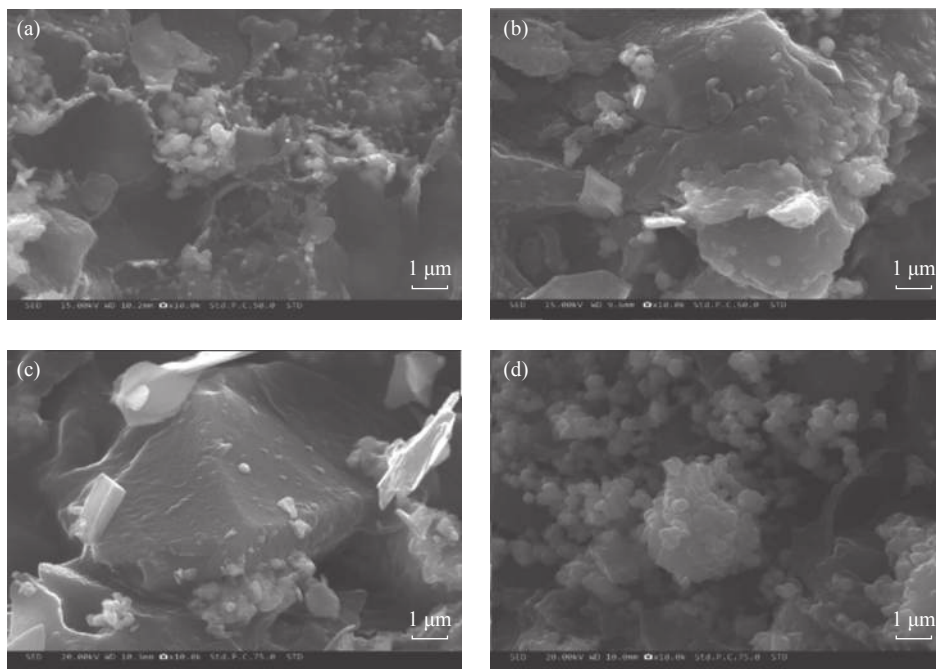


图2 (a)PS、(b)CC、(c)PSC和(d)CCC的SEM图像

Fig. 2 SEM images of (a) PS, (b) CC, (c) PSC and (d) CCC

两种生物炭表面均有一定的孔隙,可以观察到CC表面比PS表面有更多的孔隙和凸起,说明CC与污染物有更大的接触面积,这更有利于对重金属的吸附。采用比表面积分析仪对材料的比表面积和孔径进行分析,结果显示CC的比表面积($12.045\text{m}^2/\text{g}$)和平均孔径(3.614nm)均大于PS的比表面积($3.294\text{m}^2/\text{g}$)和平均孔径(3.067nm)。

图2中c和d分别是PSC和CCC的SEM图。PSC和CCC表面均凹凸不平,有很多凸起的球形颗粒,颗粒的粒径约为 250nm ,这些球形颗粒为 Fe_3O_4 ,说明 Fe_3O_4 成功地附着在材料表面。CCC的比表面积($4.598\text{m}^2/\text{g}$)和平均孔径(3.417nm)均大于PSC的比表面积($1.514\text{m}^2/\text{g}$)和平均孔径(2.812nm),说明生物炭的原生结构性质影响复合材料的孔隙结构。同时,从SEM图中可以看出,壳聚糖和生物炭已经显著结合在一起^[22-23]。与以往文献报道结果相比,本研究中的生物炭-壳聚糖复合材料最大程度地保留了生物炭的原始结构,使壳聚糖均匀地分布在生物炭表面^[3]。

2.1.2 XRD 表征

图3A中的a、b、c和d线分别为壳聚糖、 Fe_3O_4 、PSC和CCC的XRD衍射图。壳聚糖的衍射谱在衍射角为 $2\theta=20.1^\circ$ 处存在一个较宽的衍射峰,这个衍射峰主要是由于壳聚糖内部的分子氢键的作

用^[24-25]。b线可以看出在衍射角为 $2\theta=18.3^\circ$ 、 30.14° 、 35.48° 、 43.12° 、 53.48° 、 57.02° 、 62.62° 、 71.18° 和 74.06° 处存在衍射峰,这与 Fe_3O_4 (PDF#99-0073卡片)的衍射峰一致^[26-27]。c和d线代表的峰位置比较相似,PSC(c线)在 $2\theta=30.17^\circ$ 、 35.53° 、 43.24° 、 57.04° 和 62.61° 等五处存在衍射峰,CCC(d线)在 $2\theta=26.63^\circ$ 、 30.08° 、 35.44° 、 43.03° 、 57.07° 和 62.55° 处存在衍射峰,它们对应于JCPDS数据库中PDF#99-0073(Fe_3O_4)的衍射峰(35.426° 、 62.520° 、 56.935° 、 30.076° 和 43.053°),这些衍射峰对应的晶面衍射分别为(311)、(440)、(511)、(220)、(400)和(731),表明将磁性因子 Fe_3O_4 成功地嵌入复合材料中。值得注意的是,PSC和CCC衍射图中没有其他的杂质衍射峰,且形成的衍射峰相对清晰,说明磁性复合材料的制备是成功的。

2.1.3 溶胀性表征

选取了三种pH值(4、7和10)对材料的溶胀性进行评价,实验结果见图3B。从图中看出两种材料在三个pH值条件下的溶胀比相差不大,且均未超过100.0%,表现出较高的稳定性,这是由于生物炭作为载体具有较好的支撑作用^[22]。在pH=7时CCC和PSC的溶胀比最大,分别为58.8%和80.5%,说明CCC和PSC在中性条件下不稳定。前人研究发现壳聚糖易溶于酸性溶液,表明采用本研究制备的

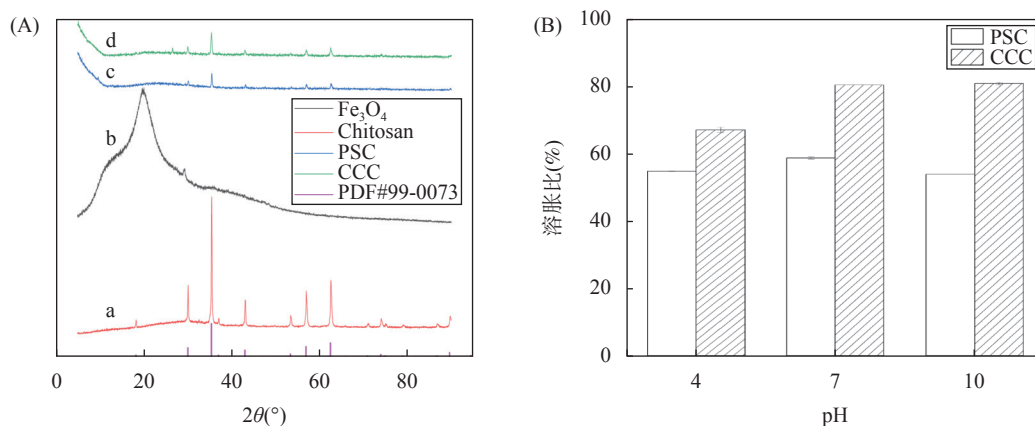


图3 (A)Fe₃O₄(a线)、壳聚糖(b线)、CCC(c线)、PSC(d线)的XRD谱图; (B)材料在不同pH条件下(4、7、10)的溶胀性
Fig. 3 (A) XRD patterns of Fe₃O₄ (line a), chitosan (line b), CCC (c line) and PSC (d line); (B) Swelling properties of materials under different pH conditions (pH=4, 7, 10).

材料经改性后增强了壳聚糖在酸性条件下的稳定性。同时相较于使用氨基硫脲改性壳聚糖材料的溶胀比(1320.0%)^[28], 本研究中的材料具有较低的溶胀比和较强的稳定性。

2.2 初始 pH 的影响

溶液初始 pH 对材料吸附的影响见图 4。在初始 pH=7 时 PSC 和 CCC 对 Pb²⁺ 的最大吸附容量均为 12.36mg/g, 对 Cu²⁺ 的最大吸附容量均为 8.31mg/g。随着初始 pH 值从 3 增加至 7, 材料的吸附容量和去除率不断增大, 这是由于随着初始 pH 值的增加, 吸附剂表面的正电荷减少, 降低了材料表面与溶液中

Pb²⁺ 和 Cu²⁺ 的静电斥力, 增加了材料表面与 Pb²⁺ 和 Cu²⁺ 之间的静电引力, 而静电引力的增加有利于 Pb²⁺ 和 Cu²⁺ 的吸附^[29-30]。在 pH 为 2~3 时, PSC 和 CCC 对 Pb²⁺ 和 Cu²⁺ 的吸附容量均较低, 这可能是由于吸附剂表面发生了质子化, 更多的—NH₂ 转化为 NH₃⁺, 材料表面与金属阳离子的静电斥力增强, 使吸附容量减少^[25]。与同类型的壳聚糖/猕猴桃生物炭相比, 在 pH 4~7 范围内本研究的两种吸附剂均表现出相对稳定的吸附性能, 说明本研究制备的吸附剂具有更广泛的 pH 值适用范围^[31]。

2.3 吸附动力学和等温线模型拟合

采用伪一级和伪二级动力学模型对动力学数据进行拟合, 伪一级和伪二级动力学模型如公式(3)和(4)所示^[32-33]。采用 Langmuir 和 Freundlich 等温线模型对数据进行拟合, 两种等温模型如公式(5)和(6)所示^[14,33]。

(1) 伪一级动力学模型

$$q_t = q_e [1 - e^{-k_1 t}] \quad (3)$$

式中: q_t 为 t 时刻吸附剂的吸附量(mg/g); q_e 为吸附达到平衡时吸附剂的吸附量(mg/g); k_1 代表速率常数(min⁻¹); t 为反应时间(h)。

(2) 伪二级动力学模型

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (4)$$

式中: q_t 为 t 时刻吸附剂的吸附量(mg/g); q_e 为吸附达到平衡时吸附剂的吸附量(mg/g); k_2 代表速率常数 [g/(mg·min)]; t 为反应时间(h)。

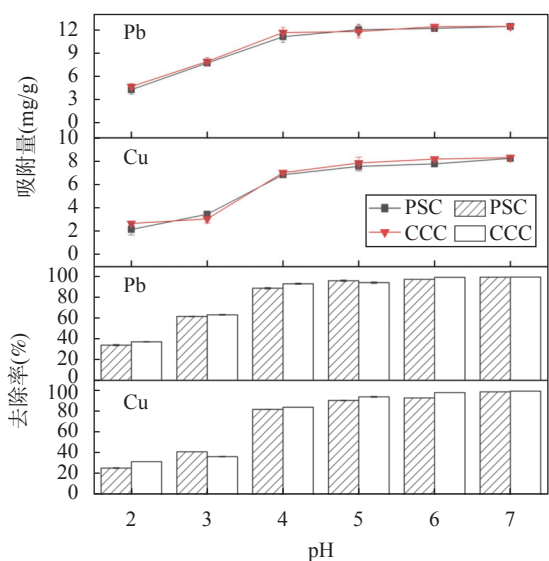


图4 pH 对 PSC 和 CCC 吸附 Cu²⁺ 和 Pb²⁺ 效果的影响
Fig. 4 Effect of pH on adsorption of Cu²⁺ and Pb²⁺ by PSC and CCC (Dosage=4g/L, initial concentration of Cu²⁺ and Pb²⁺ are both 50mg/L).

(3) Langmuir 等温模型

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

式中: q_e 是平衡时的吸附容量(mg/g); q_m 是最大吸附容量(mg/g); K_L 是 Langmuir 常数(L/mg); C_e 代表平衡时溶液中吸附质的浓度(mg/L)。

(4) Freundlich 等温模型

$$q_e = K_F C_e^{\frac{1}{n}} \quad (6)$$

式中: q_e 是平衡时的吸附容量(mg/g); K_F 是 Freundlich 常数(L/mg); C_e 代表平衡时溶液中吸附质的浓度(mg/L); n 代表与吸附强度有关的参数。

材料吸附 Pb^{2+} 和 Cu^{2+} 的动力学拟合参数见表 1。 k_2 反映了吸附达到平衡状态的速率, k_2 值越大, 吸附达到平衡的速度越快。从表 1 中可以看出, PSC 和 CCC 在吸附 Pb^{2+} 时, 达到平衡的速度 $PSC > CCC$; 在吸附 Cu^{2+} 时, 达到平衡的速度 $CCC > PSC$ 。PSC 和 CCC 吸附 Pb^{2+} 时, 两种材料的伪一级与伪二级动力学模型相比, 伪一级动力学模型的 R^2 值更高且 χ^2 值更低, 说明 PSC 和 CCC 吸附 Pb^{2+} 的过程符合伪一级动力学模型, 在吸附过程中物理吸附占主导作用^[10]。PSC 和 CCC 在吸附 Cu^{2+} 时, 两种材料的伪一级与伪二级动力学模型相比, 伪二级动力学模型的 R^2 值更高且 χ^2 值更低, 说明伪二级动力学可以更好地拟合此吸附过程, 化学吸附主导了此吸附过程^[23]。

材料吸附等温线模型的拟合相关计算参数见表 1。当初始浓度从 10mg/L 增加到 500mg/L 时, PSC 对 Pb^{2+} 的吸附量分别从 2.5mg/g 增加至 56.32mg/g, 对 Cu^{2+} 的吸附量从 1.67mg/g 增加至 16.68mg/g, 这

是由于随着初始浓度的提高, 溶液中金属离子与吸附剂表面的浓度梯度增大, 因而增强了溶液中金属离子到吸附剂表面的驱动力, 进而提高了传质效率^[34]。吸附等温线拟合结果显示, CCC 对 Pb^{2+} 和 Cu^{2+} 的最大理论吸附容量分别为 169.10mg/g 和 18.69mg/g, PSC 对 Pb^{2+} 和 Cu^{2+} 的最大理论吸附容量分别为 86.72mg/g 和 14.34mg/g。由于 CCC 对 Pb^{2+} 和 Cu^{2+} 的最大理论吸附容量比 PSC 高, 在处理实际含 Pb^{2+} 和 Cu^{2+} 的废水时可优先选择 CCC 作为吸附剂。与 Freundlich 等温吸附模型相比, 两种材料对 Pb^{2+} 和 Cu^{2+} 的吸附过程均更加符合 Langmuir 等温吸附模型, 这表明材料表面的吸附位点是均匀的, 且吸附过程为单层吸附^[34-35]。

本研究的两种材料与其他材料吸附容量的比较见表 2。从表中数据可知, 本研究的材料对 Pb^{2+} 的吸附容量相比其他材料具有一定的优势, 对 Cu^{2+} 的吸附容量与其他材料相比较差, 但本研究的材料可同时吸附 Pb^{2+} 和 Cu^{2+} 两种离子, 在实际应用中可考虑将 Pb^{2+} 作为主要目标污染物。

2.4 材料循环利用性

一般吸附剂吸附金属阳离子后使用酸性溶液进行脱附, 酸性条件下材料表面带正电荷, 利用静电斥力将吸附到材料表面的金属离子进行脱附, 酸性溶液如盐酸、硝酸和硫酸等^[6]。由于壳聚糖易溶于酸性溶液, 因此本研究采用螯合能力较强的 EDTA-2Na 作为壳聚糖复合材料的脱附剂^[17]。循环实验结果如图 5 所示, 随着循环次数的增加, 材料对 Pb^{2+} 和 Cu^{2+} 的去除率下降, 这可能是由于脱附时未将材料表面上吸附的 Pb^{2+} 和 Cu^{2+} 完全脱附, 从而增加材料表

表 1 PSC 和 CCC 吸附 Pb^{2+} 、 Cu^{2+} 动力学模型拟合参数以及 PSC 和 CCC 吸附 Pb^{2+} 、 Cu^{2+} 等温线模型拟合参数

Table 1 Fitting parameters of kinetic models for Pb^{2+} and Cu^{2+} adsorption by PSC and CCC, and the fitting parameters of PSC and CCC adsorption of Pb^{2+} and Cu^{2+} isotherm models.

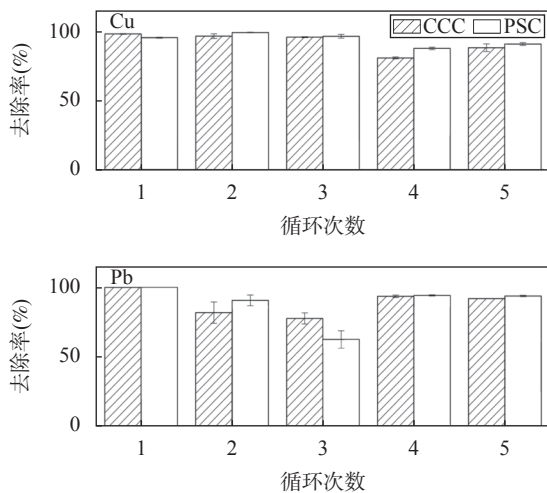
金属离子	制备材料	伪一级动力学模型			伪二级动力学模型				
		K_1	R^2	χ^2	k_2	R^2	χ^2		
Pb^{2+}	PSC	0.0375	0.998	0.042	0.0062	0.936	0.114		
	CCC	0.0045	0.999	0.044	0.0004	0.986	0.121		
Cu^{2+}	PSC	0.0072	0.996	0.049	0.0009	0.997	0.135		
	CCC	0.0037	0.988	0.082	0.0021	0.997	0.056		
金属离子	制备材料	Langmuir 模型				Freundlich 模型			
		q_m	K_L	R^2	χ^2	K_F	$1/n$	R^2	χ^2
Pb^{2+}	PSC	189.09	0.0017	0.999	0.702	0.766	0.749	0.992	8.460
	CCC	86.72	0.0036	0.998	1.420	1.220	0.622	0.984	9.706
Cu^{2+}	PSC	18.69	0.0123	0.981	0.973	1.277	0.419	0.952	2.372
	CCC	14.34	0.0197	0.979	0.667	2.72	0.368	0.928	0.375

表2 PSC和CCC吸附Pb和Cu的性能与其他材料对比

Table 2 Comparison of the adsorption capacities of PSC and CCC with other materials.

吸附剂	最大吸附容量(mg/g)		参考文献
	Pb	Cu	
二甘酸功能化磁性壳聚糖	70.57	-	[36]
EDTA-改性壳聚糖/SiO ₂ /Fe ₃ O ₄	123.5	44.4	[37]
磁性花生壳	28.3	-	[38]
磁性壳聚糖/纤维素微球	45.8	88.2	[39]
介孔CoFe ₂ O ₄ 纳米颗粒	32.1	-	[40]
CCC	169.10	18.69	本研究
PSC	86.72	14.34	本研究

注:“-”表示文献中未提供数据。

图5 PSC和CCC对(a)Pb²⁺和(b)Cu²⁺的循环利用性Fig. 5 The recycling of (a)Pb²⁺ and (b)Cu²⁺ by PSC and CCC.

面与溶液中金属离子之间的静电斥力,减少了材料表面的吸附位点^[22]。在循环5个周期后对Pb²⁺和Cu²⁺的去除率仍在85%以上,这一结果表明本研究中的两种吸附剂具有优异的稳定性和可循环的环保型吸附材料。

2.5 实际地下水实验

由于CCC对Pb²⁺和Cu²⁺的吸附容量大于PSC,因此采用CCC对实际地下水进行处理。实际矿山地下水中含有As、Cd、Cu、Fe、Mn、Ni、Ca和Na。在吸附后,As、Cd、Cu、Fe、Mn和Ni浓度分别从18.200、3.800、13.300、21500.000、510.000和87.000μg/L降低至0.479、0.003、1.490、173.000、493.000和8.000μg/L,去除率分别为97.36%、99.92%、91.8%、99.92%、3.33%和90.81%,这表明材料对这些金属离子均有一定的吸附作用。可以观察到,CCC对Cd和Fe的去除率最高(99.92%),对Mn的

去除率最低(3.33%),建议对含Mn重金属复合污染的水体使用本材料进行处理时,增加单独除Mn工艺模块。在吸附前后,Ca²⁺浓度从40.541mg/L增加至68.647mg/L,Na²⁺浓度从81.694mg/L增加至95.647mg/L,这可能由于材料自身的溶出或CCC在吸附Cu²⁺的过程中与Zn²⁺、Ca²⁺和Na²⁺发生了离子交换^[41-43]。吸附后Cu²⁺的浓度从13.30mg/L降低至1.09mg/L,去除率为91.8%,其浓度达到《地下水质量标准》IV类水标准,但去除率小于用去离子水配制的含Cu²⁺污染水,这是因为实际水体中存在其他的金属阳离子,这些金属阳离子会与Cu²⁺竞争材料表面的吸附位点。以上结果表明,本研究中的CCC材料可有效地去除实际地下水中的多种金属离子。

2.6 材料吸附前后表面官能团分析

图6中a、b和c分别是PSC、吸附Pb²⁺后的PSC和吸附Cu²⁺后的PSC的XPS N1s图,其中PSC的N1s存在5个峰,位于398.6、399.2、399.7、401.0和403.8eV处,分别是吡咯类的氮(—NH)、壳聚糖的氨基(—NH₂)、C=N、NH₃⁺和C—N,在吸附Pb²⁺后,峰位置变为398.6、399.3、399.8和399.9eV^[3,44],可以明显观察到C—N峰的消失,说明C—N参与了吸附过程。吡咯类的—NH和—NH₂峰明显减弱,说明这两个含氮官能团也参与了PSC吸附Pb²⁺的过程。PSC吸附Cu²⁺后,C=N的峰明显减弱,其他峰变化与吸附Pb²⁺相似,说明C—N、—NH、—NH₂和C=N也参与了Cu²⁺的吸附过程。

图6中d、e和f分别是CCC、吸附Pb²⁺后的CCC和吸附Cu²⁺后的CCC的XPS N1s图。在吸附Pb²⁺前,CCC的N1s存在3个峰,位于398.7、398.9.2和399.5eV处,分别是吡咯类的氮(—NH)、壳聚糖的氨基(—NH₂)和C=N。在吸附Pb²⁺后,峰变为4个,新出现的峰为402.5eV处的NH₃⁺^[45]。同时,—NH₂峰减弱程度相比其他峰较小,可能是在吸附Pb²⁺的过程中参与不明显,反应生成了部分的NH₃⁺。CCC吸附Cu²⁺后峰强均减弱,说明CCC本身的吡咯类的氮(—NH)、壳聚糖的氨基(—NH₂)和C=N均参与了CCC吸附Cu²⁺的过程^[31]。XPS分析结果表明,PSC和CCC在吸附Pb²⁺和Cu²⁺过程中材料表面的含氮官能团起到了重要作用,含氮官能团主要通过金属离子螯合作用,即金属离子与N原子形成共价键,达到吸附Pb²⁺和Cu²⁺的目的^[18]。

3 结论

本研究制备了两种生物炭-壳聚糖磁性复合吸附剂PSC和CCC,SEM和BET表征显示生物炭的

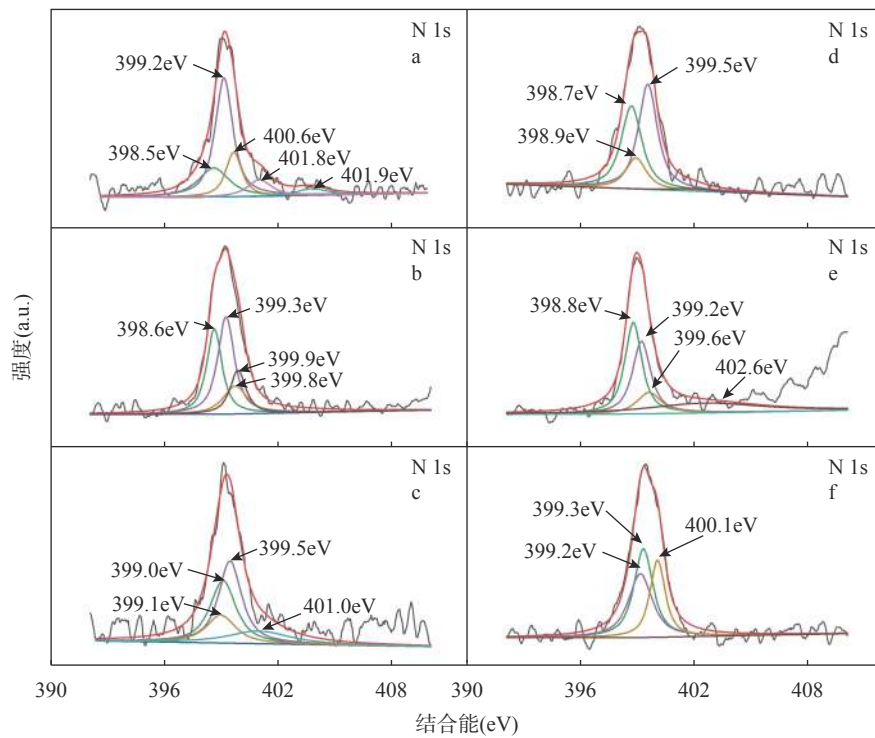


图6 PSC(a)、吸附 Pb^{2+} 后PSC(b)、吸附 Cu^{2+} 后PSC(c)、CCC(d)、吸附 Pb^{2+} 后CCC(e)、吸附 Cu^{2+} 后CCC(f)的XPS谱图
Fig. 6 XPS spectra of PSC (a), PSC after Pb^{2+} adsorption (b), PSC after Cu^{2+} adsorption (c), CCC (d), CCC after Pb^{2+} adsorption (e), CCC after Cu^{2+} adsorption (f).

原始结构影响着复合材料的孔隙特征,原始生物炭的比表面积和孔径越大,复合材料的比表面积和孔径越大。同时这两种吸附剂均对溶液中 Pb^{2+} 和 Cu^{2+} 具有良好的吸附能力,PSC和CCC对 Pb^{2+} 的吸附过程以物理吸附为主,对 Cu^{2+} 的吸附过程以化学吸附为主。PSC和CCC对 Pb^{2+} 和 Cu^{2+} 的吸附均为单层吸附。CCC对 Pb^{2+} 和 Cu^{2+} 的最大理论吸附容量分别为169.10mg/g和18.69mg/g,PSC对 Pb^{2+} 和 Cu^{2+} 的最大理论吸附容量分别为86.72mg/g和14.34mg/g。

pH影响实验和XPS结果表明静电吸引和螯合作用是 Pb^{2+} 和 Cu^{2+} 的主要吸附机制。

本研究中材料的制备方法有效地提升了壳聚糖类材料在不同pH条件下的适应性。CCC对实际地下水中的多种重金属离子具有良好的去除能力。本研究主要针对的重金属是非变价金属离子 Pb^{2+} 和 Cu^{2+} ,建议后续可以研究生物炭-壳聚糖材料对变价金属离子的去除,以拓展生物炭-壳聚糖材料的应用场景。

Preparation and Application of Biochar-Chitosan Magnetic Composite Adsorbent for Removal of Lead and Copper from Groundwater

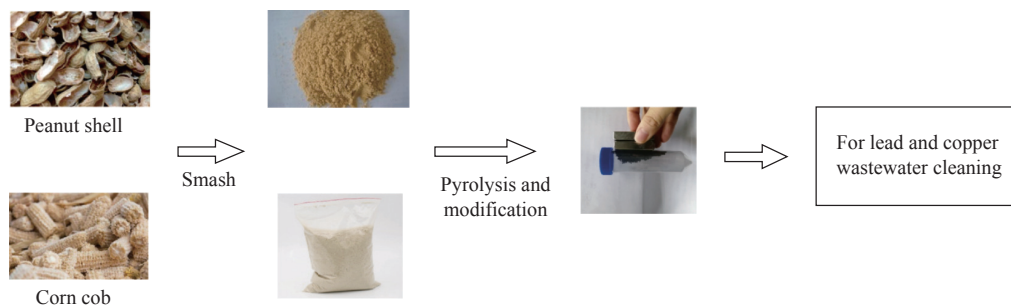
YANG Mengnan¹, SUN Han¹, CAO Hailong¹, JIA Zenghua¹, FENG Zhengyuan², ZHENG Lijun², CHEN Nan^{2*}

(1. Land and Environment Rehabilitation Center, China GEO-Engineering Corporation, Beijing 100093, China;

2. School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing 100083, China)

HIGHLIGHTS

- (1) The combination of peanut shell/corn cob biochar with chitosan improves the adaptability of chitosan materials to solutions of different pH values.
- (2) Biochar-chitosan magnetic composites remove heavy metals mainly through electrostatic attraction and chelation of nitrogen-containing functional groups.
- (3) Biochar-chitosan magnetic composite can effectively remove Cu^{2+} , Pb^{2+} , Cd^{2+} and Fe^{3+} from groundwater.



ABSTRACT

BACKGROUND: Wastewater containing heavy metals produced by mining, beneficiation, smelting, forging, processing, transportation, and other industries that has been improperly disposed of, leads to heavy metals entering and polluting the groundwater environment. Heavy metals can be enriched in the human body and participate in the biological cycle. Long-term accumulation of heavy metals in the human body will bring carcinogenic, teratogenic, and mutagenic risks. Adsorption has been of wide concern in the treatment of heavy metals pollution in water, due to the advantages of low operation cost, simple engineering operation and low secondary pollution. Chitosan as a natural organic polysaccharide organic matter, has the characteristics of being environmentally friendly. It contains many nitrogen-containing functional groups that can adsorb metal ions in water. However, the adaptability of chitosan adsorbents to acidic conditions is poor, so the pH value needs to be adjusted in the actual process, which increases the operating cost. Combining biochar with chitosan can not only improve the adsorption capacity of chitosan, but also improve the separation performance of biochar. However, most of the research on chitosan modified biochar concentrate on the single biochar. There are few studies on the modification of biochar from different sources by chitosan, and the interaction between chitosan and biochar is not clear.

OBJECTIVES: The aim of this study was to prepare peanut shell biochar-chitosan magnetic composite adsorbent (PSC) and corn cob biochar-chitosan magnetic composite adsorbent (CCC), and to investigate the $\text{Pb}^{2+}/\text{Cu}^{2+}$ adsorption properties and mechanisms on PSC and CCC.

METHODS: Scanning electron microscope was used to analyze the microstructure of the material, and the material samples were treated with gold spray before photographing. The specific surface area and pore volume of the material were determined using a specific surface area analyzer, and the material was adsorption-desorption tested with nitrogen at -196°C . X-ray diffraction was used to analyze the crystal structure of materials, and the Cu $K\alpha$ source was used to scan in the range of 10° - 80° (2θ). X-ray photoelectron spectrometer was used to analyze the changes of functional groups on the surface of the material, and the radiation (225W, 15mA, 15kV) was carried out by monochromatic Al- $K\alpha$. Metal ion content in solution was measured by inductively coupled plasma-optical emission spectrometry.

The adsorption experiments were carried out in a 50mL conical flask and a constant temperature shaker. The oscillation frequency was 150r/min and the reaction time was 12h. After the reaction, the concentrations of Pb^{2+} and Cu^{2+} in the solution were determined. Two parallel samples were set up in each group. Different initial pH experiments were used to evaluate the adsorption performance of materials. Kinetic and isothermic models were used to evaluate the adsorption kinetic process of materials and predict the maximum adsorption capacity of materials. Recycling experiments and actual mine groundwater adsorption experiments were used to evaluate the practical application capacity of materials.

RESULTS: SEM images of PS and CC showed that there were many pores on the surface of both types of carbon. There were more pores and bulges observed on the surface of CC than PS, indicating that CC had a larger contact area with pollutants than PS. The specific surface area ($12.045\text{m}^2/\text{g}$) and mean pore diameter (3.614nm) of CC were larger than those of PS (specific surface area was $3.294\text{m}^2/\text{g}$ and mean pore diameter was 3.067nm), which was consistent with the SEM results. The specific surface area ($4.598\text{m}^2/\text{g}$) and average pore diameter (3.417nm) was 2.812nm), indicating that the primary structural properties of biochar affected the pore structure of the composites. SEM of CCC and PSC showed that chitosan and biochar were well combined. Compared with previous literature, the biochar-chitosan composite material in this study preserves the original structure of biochar to the greatest extent, and makes the chitosan evenly coated on the surface of biochar. The results BET showed that the primary structural properties of the biochar affected the physical properties of the modified materials. The XRD results showed that Fe_3O_4 was successfully embedded into the composite material. Three pH values (4, 7 and 10) were selected to evaluate the swelling properties of the materials. The results showed that the swelling ratios of the two materials were similar under the three pH conditions, and neither of them was more than 100.0%, which was due to the biochar as a carrier having a good supporting effect. Compared with chitosan/kiwifruit branch biochar adsorbent, the two adsorbents in this study showed relatively stable adsorption properties in the pH range of 4-7, indicating that the adsorbents had a wider range of pH value application.

The effect of the initial pH on the adsorption was tested. As the initial pH value increased from 3 to 7, the adsorption capacity and removal efficiency of the material increased. The positive charge of the adsorbent surface also decreased, which reduced the electrostatic repulsion of Pb^{2+} and Cu^{2+} between the material surface and the solution, and increased the electrostatic attraction between the material surface and Pb^{2+} and Cu^{2+} . The increasing electrostatic attraction was beneficial to the adsorption of Pb^{2+} and Cu^{2+} . When PSC and CCC adsorbed Pb^{2+} , the pseudo-first-order kinetic model could better describe the adsorption process than the pseudo-second-order kinetic model, indicating that physical adsorption played a dominant role in the adsorption of Pb^{2+} by PSC and CCC. Pseudo-second-order kinetics can better fit the Cu^{2+} adsorption by PSC and CCC than pseudo-second-order kinetic model, indicating that chemisorption dominates the adsorption process of Cu^{2+} by PSC and CCC. The Langmuir isotherm adsorption model can better describe the adsorption process of Pb^{2+} and Cu^{2+} than Freundlich isotherm

adsorption model, indicating that the adsorption process is monolayer adsorption.

The EDTA-2Na was used as the desorption agent of chitosan composite, the removal efficiencies of Pb^{2+} and Cu^{2+} were still above 85% after five cycles, which indicated that the two adsorbents in this study had excellent stability. PSC and CCC were the low-cost and effective adsorption materials. Groundwater of an acid mine was taken from a mining area in Dongshan District, Dafan Mountain, Anhui Province. The groundwater samples contained large amounts of metal ions, such as As, Ca, Cd, Cu, Fe, Mn, Na and Ni, the corresponding concentrations were 18.200 $\mu\text{g/L}$, 40.541 mg/L , 3.800 $\mu\text{g/L}$, 13.300 mg/L , 215.00 mg/L , 510.00 $\mu\text{g/L}$, 81.694 mg/L and 87.000 $\mu\text{g/L}$, respectively. 0.45 μm filter membrane was used to remove particulate impurities from the water before adsorption. CCC was used to treat the heavy metal polluted groundwater, and the results showed that CCC has a good removal ability on a variety of metal ions in groundwater such as Cu^{2+} , Cd^{2+} , and Fe^{3+} . The Cu^{2+} concentration in the treated water can reach the Grade IV water standard of the “Groundwater Quality Standard”.

The pH results showed that the removal mechanisms of Pb^{2+} and Cu^{2+} by PSC and CCC mainly included electrostatic attraction. The functional groups of adsorbents before and after adsorption were analyzed through X-ray photoelectron spectroscopy (XPS). The results of XPS showed that complexation was another removal mechanism. The nitrogen ($-\text{NH}$) of pyrroles, amino of chitosan ($-\text{NH}_2$), and $\text{C}=\text{N}$ were the main functional groups, which were responsible for the complexation with Pb^{2+} and Cu^{2+} .

CONCLUSIONS: The preparation method of the materials in this study can effectively improve the adaptability of chitosan materials under different pH conditions. The adsorbents developed in this study can effectively remove heavy metals from groundwater and have a good application potential.

KEY WORDS: biochar; chitosan; adsorption; lead; copper; N-containing functional groups; X-ray photoelectron spectroscopy

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