



风化煤提取的胡敏酸对镉的吸附性能及其应用潜力

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摘要 以“碱溶酸析”法从新疆风化煤中提取的胡敏酸为研究对象,对其理化性质和表面形态进行表征,并通过吸附试验探究反应时间、溶液 pH、镉离子(Cd²⁺)质量浓度对胡敏酸吸附 Cd²⁺的影响.结果表明:风化煤提取的胡敏酸碳元素质量分数高达 58.68%,羧基的质量摩尔浓度为 5.81 mol/kg,等电点为 2.7;该胡敏酸含 Cd 量为 0.15 mg/kg,符合国家土壤环境质量标准.胡敏酸对 Cd²⁺的吸附在 8 h 内达到平衡,吸附量随 Cd²⁺质量浓度(0~100 mg/L)和溶液 pH 升高而增加,到 pH=6.0 时最大,之后胡敏酸开始溶解导致吸附量降低.Langmuir 方程比 Freundlich 方程能更好地拟合胡敏酸对 Cd²⁺的吸附等温线,显示出单分子层吸附的特点.在 pH=5.0 时,胡敏酸对 Cd²⁺的饱和吸附量达 137.37 mg/g,相当于用去了酸度系数(pK_a)为 3 的羧基含量的 71%.在 pH=4.3、Cd²⁺初始质量浓度为 80 mg/L 的同等条件下,新疆风化煤提取的胡敏酸对 Cd²⁺的吸附量为 86.97 mg/g,高于国际腐殖质协会胡敏酸标样 1R106H 对 Cd²⁺的吸附量(73.49 mg/g).风化煤来源广、储量大、价格低,以它为原料制备获得的胡敏酸产量高、吸附能力强、环境友好、施用安全,有望作为吸附剂用于含重金属废水处理,以及作为钝化剂和土壤调理剂用于重金属污染土壤的修复.

关键词 镉; 胡敏酸; 吸附; 风化煤; 污染土壤
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Humic acid from Leonardite for cadmium adsorption and potential applications. *Journal of Zhejiang University (Agric. & Life Sci.)*, 2016, 42(4):460-468

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Summary Cadmium (Cd) is a toxic and carcinogenic contaminant released from a wide range of industries. Its accumulation in soil and water is of growing environmental and health concerns. Thus, there is an increasing

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demand for materials that are effective for Cd adsorption, economically feasible, and unlikely to create new environmental problems.

Humic acid (HA) is ubiquitous in soil and sediment. It can also be extracted from lignite and leonardite, which can be viewed as ancient biochar and oxidized ancient biochar, respectively. Being abundant in carboxyl and hydroxyl groups ($-\text{COOH}$, $-\text{OH}$), HA has a strong propensity for adsorbing heavy metal cations by forming inner-sphere complexes, thus reducing their mobility and bioavailability. A leonardite (Leo) from Xinjiang, China was used to produce HA by ultrasonically dispersing Leo in 0.1 mol/L NaOH solution at 40 °C for 30 min, and then flocculating the supernatant with 6 mol/L HCl. The obtained HA (Leo-HA) was characterized for its surface properties by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR), and was analyzed for elemental compositions, carboxyl group, and isoelectric point (pI). Further, its adsorption characteristics were determined by kinetic and batch experiments, and its potential applications in removing Cd^{2+} from water and immobilizing Cd^{2+} in soils were assessed based on its technical reliability, economic feasibility, and environmental impact. For environmental relevance, a relatively low range of Cd^{2+} concentrations (0-100 mg/L) was used in adsorption experiment, during which the pH of solution was maintained constant.

Results showed that Leo-HA had a low pI of 2.7 and a high C content of 58.68%, which is not unusual for coal-derived HA. FTIR confirmed the abundance of $-\text{COOH}$ and $-\text{OH}$ groups. The carboxyl group was determined at 5.81 mol/kg. The low Cd concentration (0.15 mg/kg) of Leo-HA met the prerequisite for safe use in agricultural land, as regulated by Farmland Environmental Quality Standards. Kinetic studies showed that Cd^{2+} adsorption onto Leo-HA reached equilibrium in 8 h and the process was pH-dependent. The adsorption increased with pH within 2.0-6.0, and then decreased as pH further increased to 7.0. This is because Leo-HA starts to dissolve as solution pH approaches to neutral. Adsorption data were better fitted into Langmuir equation ($R^2 = 0.991$) than Freundlich equation ($R^2 = 0.891$), suggesting the monolayer nature of Cd^{2+} adsorption onto Leo-HA. At pH 5.0, the maximum adsorption capacity (Q_m) derived from the Langmuir equation was 137.37 mg/g, which was equivalent to 71% of the carboxyl groups of Leo-HA. This Q_m was much higher than what had been reported in the literature for lignite, lignite-derived HA, and soil HA. A simple comparison at pH 4.3 and an initial Cd^{2+} concentration of 80 mg/L showed that the Leo-HA adsorbed more Cd^{2+} (86.97 mg/g) than the reference HA 1R106H (73.49 mg/g) from IHSS did, even though the later had a higher carboxyl content (6.82 mol/kg). This apparent discrepancy was due to the fact that dissolution of 1R106H was observed at pH 4.3, whereas the Leo-HA was stable at this pH.

Leonardite is abundant across China. Leo-HA has the advantages of low cost, high adsorption capacity, and low Cd content, thus it is a prospective adsorbent for immobilizing Cd^{2+} in contaminated soils or removing Cd^{2+} from water. Lime has widely been used to immobilize Cd^{2+} in soils, but it tends to reduce soil organic matter content, damage soil structure, and pose a hazard to the safety of its users in the field. In contrast, Leo-HA is beneficial to soil structure and soil quality, as well as safe to handle in the field. Field trials of applying Leo-HA onto heavy metal contaminated soils would be a logical step to follow.

Key words cadmium; humic acid; adsorption; leonardite; contaminated soil

环境保护部和国土资源部 2014 年联合公布的《全国土壤污染状况调查公报》显示,我国土壤污染总超标率为 16.1%,污染类型以无机型为主;无机污染物超标点位占全部超标点位的 82.8%,其中,镉(Cd)是首要的重金属污染物^[1].不合理的矿山开采和冶炼、金属电镀、磷肥施用和铅镉蓄电池处理等是产生 Cd 污染的重要原因^[2].我国生活饮用水对 Cd 的最大允许值是 0.005 mg/L,然而,我国水体环境状况总体不容乐观,长江、黄河等七大水系均受到不同程度

的重金属污染^[3-9].Cd、Pb 等重金属可通过饮用水和食物链进入人体,严重威胁人体健康^[10-11].因此,研究和制备符合性能稳定可靠、不产生新的环境问题、经济可行 3 个条件的吸附材料^[12]用于重金属污染水体和土壤的修复既重要又紧迫.

近 10 年来,生物质炭作为一种新型环保材料在污染物吸附及污染水体和土壤修复方面受到重视,从制备技术和吸附性能到应用前景和限制因素等都已有很好的分析和讨论^[13-15].目前,商品化的生物

质炭供应有限,价格偏高,使其大规模的应用受到限制.从实际应用角度考虑,生物质炭的物料来源需要拓宽,制备过程需要改进,与其他产业的共通互联需要加强.

生物质炭是生物质在缺氧条件下经热解过程脱气、排液而产生的固体物质,常作为土壤调理剂使用.煤是古代生物质(泥炭)在挤压、增温、缺氧条件下经地质热解过程脱水、排气(甲烷)所剩的固体物.暴露于地表的煤层在氧气和水分的共同作用下转变成富含腐殖酸的风化煤.因此,广义上,煤是古老的生物质炭,风化煤是富氧的古老生物质炭,而腐殖酸则是以富氧的古老生物质炭为原料经过碱性活化的产物.

腐殖酸是工业名称,与胡敏酸大致相当,因制备条件不同可含有不同数量的富里酸.胡敏酸(humic acid, HA)是广泛存在于土壤和底泥的天然有机胶体,能和黏土矿物形成稳定的有机-矿质复合体,起到疏松土壤、保蓄水分、改良土壤理化性质等作用,是土壤生态功能的物质基础^[16].胡敏酸含有多种官能团,如羧基和羟基等.前人对胡敏酸吸附重金属的过程、机制和效果已有充分和深入的研究^[17-22].TAN总结了 Zn^{2+} 与胡敏酸反应的3种方式^[23],即 COO^- 与 Zn^{2+} 的静电吸引、 $-OH$ 与 Zn^{2+} 的络合作用及 $-COOH$ 和 $-OH$ 对 Zn^{2+} 的螯合作用.这些作用可降低重金属离子在土壤中的迁移能力和生物有效性,从而减少植物对重金属的吸收.由于风化煤来源广、国内储量大(超过1 000亿t),制备胡敏酸方法简单、阳离子交换量高,因此,胡敏酸应用于重金属污染水体和土壤修复的潜力较大.

胡敏酸吸附重金属的研究大多集中于对高浓度重金属吸附方面,在吸附过程中溶液pH未保持恒定,这些与实际应用条件明显不符.为了能够更好地弄清楚可商品化的胡敏酸对重金属的吸附能力和效果,我们利用风化煤提取的胡敏酸对低质量浓度 Cd^{2+} 进行吸附动力学试验和等温吸附试验,研究反应时间、溶液pH、重金属离子浓度对吸附的影响,评估风化煤提取的胡敏酸应用于修复重金属污染水体和土壤的可能性.

1 材料与方法

1.1 胡敏酸的制备及理化性质表征

风化煤(leonardite, Leo)原料来自新疆维吾尔自治区昌吉州奇台县一露天煤矿,其可采储量在2 000万t以上.风化煤因长期暴露于地表,其腐殖酸组分

经空气自然氧化,羧基、羟基等官能团丰度较高.

胡敏酸的制备方法:将风化煤粉末与0.1 mol/L NaOH按固液质量体积比1:10混合,在40℃恒温下超声30 min,静置24 h后将上层溶液倒出,重复提取5次,累计溶出率达90%.用6 mol/L HCl调节上述提取溶液至pH=2.0,静置絮凝、以3 000 r/min离心15 min后将上清液倒掉,沉淀物用去离子水洗3遍,去除盐分及残留富里酸后得到胡敏酸,于40℃烘干,用玛瑙研钵磨细,备用.

风化煤和胡敏酸的理化性质分析:官能团定性采用傅里叶变换红外光谱仪(FT/IR-4100,日本Jasco公司)在波长500~4 000 cm^{-1} 范围内分析;表面形态采用扫描电镜(S-400,日本日立公司)分析;元素含量采用元素分析仪(Vario Micro cube,德国Elementar公司)测定(80℃烘干样品);灰分含量是在马弗炉中经800℃煅烧4 h,根据前后质量差计算;官能团含量根据国际腐殖质协会(International Humic Substances Society, IHSS)提供的方法(www.humicsubstances.org/acidity.html)测定,将含有(0.36±0.01) g/L胡敏酸溶液的pH调节至3.0,然后用煮沸的去离子水配置的0.100 mol/L NaOH溶液滴定至pH=8.0,计算羧基含量,继续滴定至pH=10.0,计算酚羟基含量;等电点依据FERRO-GARCIA等^[24]的方法测定,将胡敏酸和风化煤分别加入到50 mL初始pH(pH_0)为2.0、3.0、4.0、5.0、6.0的0.01 mol/L KCl溶液中,并置于(25±1)℃恒温振荡器中振荡24 h后测定溶液pH,记为 pH_E ,根据 pH_0 和 ΔpH ($\Delta pH = pH_E - pH_0$)作图,在 $\Delta pH = 0$ 时的pH值即是等电点;重金属元素含量测定采用3酸(HNO_3 -HF- $HClO_4$)消解^[25],电感耦合等离子体质谱法(inductively coupled plasma mass spectrometry, ICP-MS)测定.

1.2 吸附试验

1.2.1 吸附动力学试验

称取0.549 4 g四水硝酸镉[$Cd(NO_3)_2 \cdot 4H_2O$,分析纯]用超纯水溶解定容至100 mL,溶液 Cd^{2+} 质量浓度为2 g/L,按需稀释后供吸附试验用.

向50 mL离心管中添加40 mg(精确至0.000 1 g)胡敏酸,再加入40 mL初始pH=5.0、以1 mmol/L $NaNO_3$ 为背景电解质的 $Cd(NO_3)_2$ 溶液(Cd^{2+} 质量浓度为80 mg/L).其中,1 mmol/L $NaNO_3$ 常被用来模拟湿润地区酸性土壤溶液中的离子强度.吸附试验于(25±1)℃的恒温振荡器中进行,振荡时间分别为0.25、0.5、1、1.5、2、4、8、12、24 h,每个时间

点2个平行样.振荡结束后测定pH,过0.45 μm 聚醚砜滤膜,于4 $^{\circ}\text{C}$ 条件下保存溶液.

1.2.2 pH对吸附的影响

称取30 mg(精确至0.000 1 g)胡敏酸于50 mL离心管中,分别加入40 mL以1 mmol/L NaNO_3 为背景电解质、不同pH(2.0、3.0、4.0、5.0、6.0、7.0)的 $\text{Cd}(\text{NO}_3)_2$ 溶液(Cd^{2+} 的初始质量浓度为80 mg/L),每个pH点2个平行样.吸附试验于(25 \pm 1) $^{\circ}\text{C}$ 的恒温振荡器中进行,每隔8 h用0.2 mol/L HCl或NaOH调节一次溶液pH,保持pH恒定.48 h后过0.45 μm 聚醚砜滤膜,于4 $^{\circ}\text{C}$ 条件下保存溶液

1.2.3 等温吸附试验

称取30 mg(精确至0.000 1 g)胡敏酸于50 mL离心管中,分别加入40 mL pH=5.0、以1 mmol/L NaNO_3 为背景电解质的不同初始质量浓度的 $\text{Cd}(\text{NO}_3)_2$ 溶液(Cd^{2+} 的初始质量浓度分别为0、10、20、40、60、80、100 mg/L),每个质量浓度梯度设2个平行样.吸附试验于(25 \pm 1) $^{\circ}\text{C}$ 的恒温振荡器中进行.在吸附过程中每隔8 h用0.2 mol/L HCl或NaOH调节一次溶液pH,保持pH=5.0.在48 h后过0.45 μm 聚醚砜滤膜,于4 $^{\circ}\text{C}$ 条件下保存溶液.

1.2.4 单点吸附对比试验

称取30 mg(精确至0.000 1 g)风化煤提取的胡敏酸和IHSS标样1R106H于50 mL离心管中,分别加入40 mL以1 mmol/L NaNO_3 为背景电解质、初始pH=5.0的 $\text{Cd}(\text{NO}_3)_2$ 溶液(Cd^{2+} 的初始质量浓度为80 mg/L),每个吸附材料设2个平行

样.吸附试验于(25 \pm 1) $^{\circ}\text{C}$ 的恒温振荡器中进行.在吸附过程中每隔8 h用0.2 mol/L HCl或NaOH调节一次溶液pH,保持胡敏酸和1R106H吸附溶液最终的pH相同(4.3).48 h后过0.45 μm 聚醚砜滤膜,于4 $^{\circ}\text{C}$ 条件下保存溶液.

溶液pH采用Mettler-Toledo pH计测定; Cd^{2+} 质量浓度用原子吸收分光光度计(TAS-990,北京普析通用公司)测定(标线质量浓度范围为0~1.5 mg/L).根据吸附前后溶液中 Cd^{2+} 质量浓度的变化计算胡敏酸对 Cd^{2+} 的吸附量,用平衡质量浓度和吸附量绘制吸附等温线.数据处理、绘图采用软件Origin 8.0.

2 结果与分析

2.1 供试材料的理化性质

2.1.1 元素组成和灰分含量分析

风化煤和胡敏酸的C、H、N、S和灰分含量如表1所示.作为对比,表1中列出了国际腐殖质协会从新西兰湿润地带牧区土壤——典型不饱和湿润始成土(typic Dystrudept)中提取的腐殖质标样1R106H的理化性质.胡敏酸的C含量比风化煤高,这和胡敏酸的灰分含量较低有关.新疆风化煤提取的胡敏酸的C含量比1R106H胡敏酸高,而N含量很低,反映了不同成因对胡敏酸组分的影响.2种胡敏酸都有较高的羧基(—COOH)含量,表明它们即使在酸性条件下也对金属阳离子有较强的吸附能力.

表1 风化煤和胡敏酸的理化性质

Table 1 Physical and chemical properties of leonardite and its derived humic acid

材料 Materials	pH	含水率 Moisture content/%	w(C)/ %	w(H)/ %	w(N)/ %	w(S)/ %	$m_B(\text{COOH})/$ (mol/kg) ^{a)}	w(灰分) Ash content/%
风化煤 Leo	4.21	2.94	51.90	3.01	0.81	1.43	4.46	16.64
胡敏酸 HA	4.02	24.80	58.68	2.92	0.87	1.15	5.81	7.87
IHSS 标样 IHSS standard sample	3.74	8.10 ^{b)}	54.00 ^{b)}	4.84 ^{b)}	5.13 ^{b)}	0.64 ^{b)}	6.82	1.41 ^{b)}

元素和灰分含量以干物质为基础计算。^{a)}无灰基干物质为基础计量;^{b)}无灰基样品测定(数据来自IHSS)。

Leo: Leonardite; HA: Leonardite-derived humic acid; IHSS: International Humic Substances Society. Elemental and ash compositions were calculated on dry matter mass; ^{a)}On water- and ash-free basis; ^{b)}Ash-free basis (data from IHSS).

经3酸(HNO_3 -HF- HClO_4)消解,ICP-MS测定分析得到新疆风化煤含Cd、Pb、Cu、Zn的量分别为0.15、2.81、6.51、69.56 mg/kg,风化煤提取的胡敏

酸含Cd、Pb、Cu、Zn的量分别为0.15、3.23、6.09、19.57 mg/kg,重金属含量较低,均符合HJ/T332—2006《食用农产品产地环境质量评价标准》的要求,

可以作为土壤调理剂和修复剂使用。

2.1.2 胡敏酸表面形态分析

扫描电镜照片(图1)显示,经过40℃烘干磨细的胡敏酸主要呈现2类表面形态:一类是表面较为光滑的结块,另一类是表面粗糙的多孔团聚体。胡敏酸的脱水方法可能会影响到表面形态,如WILLEY等^[26]报道冻干的胡敏酸不易结块、表面粗糙多孔;因此,不同脱水方法得到的胡敏酸是否会影响其对重金属离子的吸附动力学值得今后研究。

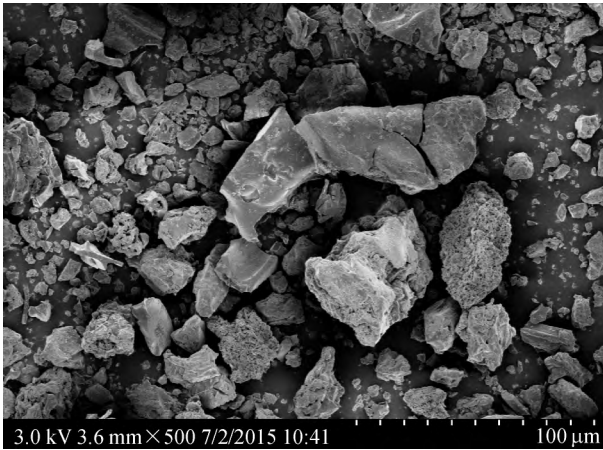


图1 胡敏酸的扫描电镜图

Fig.1 Scanning electron microscopic image of the humic acid derived from leonardite

2.1.3 傅里叶变换红外光谱分析

胡敏酸中对金属阳离子起吸附作用的主要是羧基、羟基等酸性官能团。SCHNITZER等^[27]报道,胡敏酸羧基和羟基官能团的质量摩尔浓度范围分别为2.40~5.40和1.50~4.40 mol/kg。从图2可以看出,风化煤与胡敏酸的红外光谱图相似;参考MACCARTHY等^[28]对胡敏酸类物质红外光谱图的解析,本研究供试的胡敏酸和风化煤都含有羟基(3300~3500 cm⁻¹)、羧基或羰基(1706 cm⁻¹)。

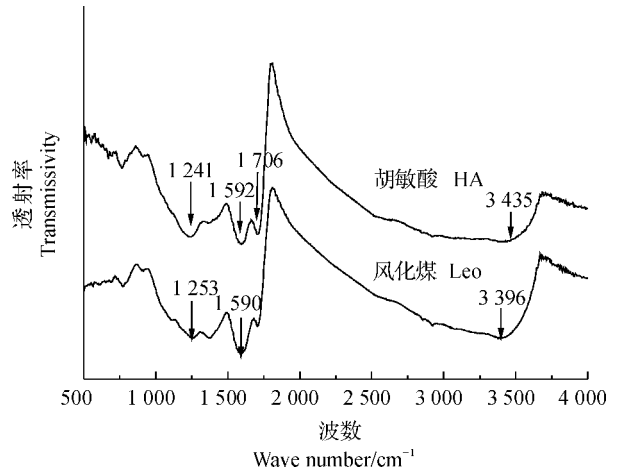
2.1.4 等电点分析

如图3所示,初始pH(pH₀)对ΔpH具有明显影响,风化煤的等电点(4.3)明显大于胡敏酸(2.7)。风化煤提取的胡敏酸结合点被氢离子结合^[21],灰分(矿物质)含量较低,从而引起胡敏酸的等电点明显小于风化煤,表明其官能团以酸性官能团为主。

2.2 胡敏酸对Cd²⁺的吸附分析

2.2.1 吸附动力学试验

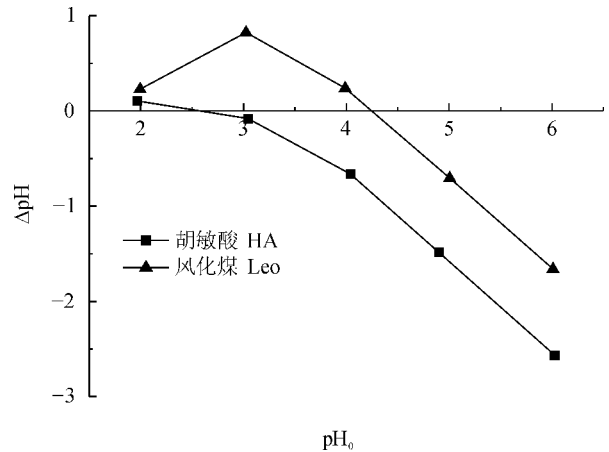
反应时间对胡敏酸吸附Cd²⁺具有明显影响,胡敏酸对Cd²⁺的吸附量随着反应时间的延长而增加,



HA: Humic acid; Leo: Leonardite.

图2 胡敏酸和风化煤的红外光谱图

Fig.2 Fourier transform infrared spectrograms of leonardite and its derived humic acid



HA: Humic acid; Leo: Leonardite.

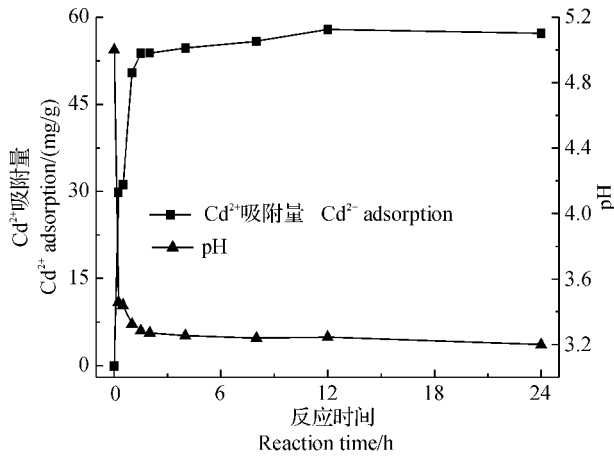
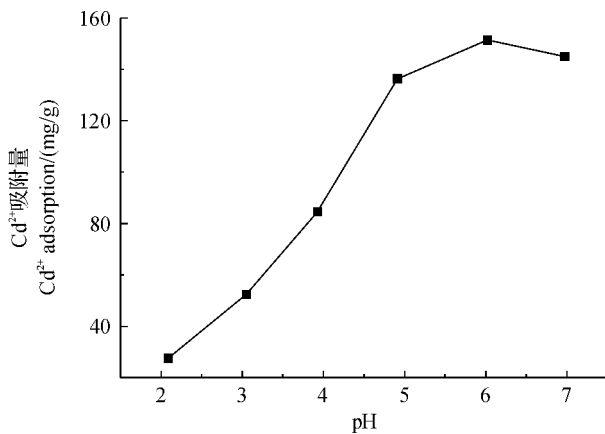
图3 风化煤与胡敏酸的等电点

Fig.3 Isoelectric points of leonardite and its derived humic acid

特别是在0~1.5 h之间吸附量明显增加,之后吸附量增加幅度减小直至吸附平衡(图4)。在吸附过程中起作用的主要是羧基官能团,因为羧基、羟基的酸度系数(pK_a)分别为pH=3.0和pH=9.0^[23],在酸性条件下羟基基本不解离。吸附试验初始,溶液的pH随着反应时间增长快速降低,之后降低幅度减小直至趋于稳定。结合吸附量和溶液pH随时间的变化,胡敏酸吸附Cd²⁺达到平衡所需时间为8 h。

2.2.2 溶液pH对胡敏酸吸附Cd²⁺的性能影响

溶液pH是控制吸附过程的关键因子之一^[22]。如图5所示,在pH<5.0时,胡敏酸对Cd²⁺的吸附量受pH影响显著,随着pH升高,胡敏酸对Cd²⁺的吸附量逐渐上升,当pH=6.0时达到最大。通常,溶

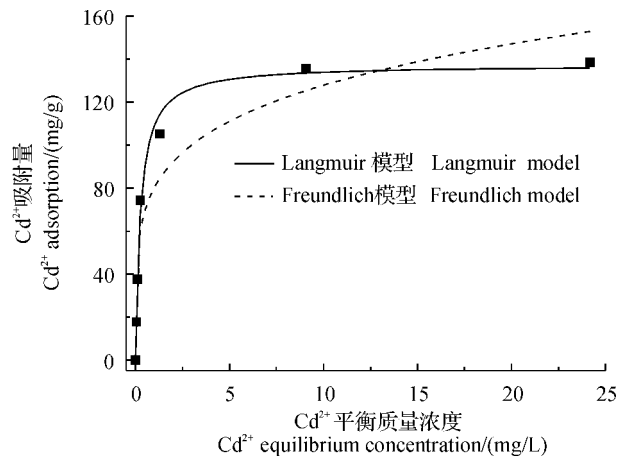
图 4 反应时间对 Cd²⁺ 吸附量和溶液 pH 的影响Fig.4 Effects of reaction time on Cd²⁺ adsorption and solution pH图 5 pH 对胡敏酸吸附 Cd²⁺ 的影响Fig.5 Effect of pH on Cd²⁺ adsorption by leonardite-derived humic acid

液 pH 升高有利于胡敏酸对阳离子的吸附^[29]. 当 pH > 6.0 时, 胡敏酸对 Cd²⁺ 的吸附量降低. 在低 pH 时, 溶液中的 H⁺、Cd²⁺ 与 COO⁻ 竞争结合; 随着溶液 pH 的升高, H⁺ 竞争减少, Cd²⁺ 的吸附增多. 当 pH = 7.0 时部分胡敏酸已经溶解, 导致固相胡敏酸质量减少, 从而降低了对 Cd²⁺ 的吸附量.

2.2.3 吸附等温线

目标重金属浓度是影响吸附反应的另一重要控制因子^[30]. 本试验通过在恒定 pH = 5.0 条件下胡敏酸对 Cd²⁺ 的吸附, 探讨胡敏酸对 Cd²⁺ 的吸附能力. 图 6 表明, 当 Cd²⁺ 的初始质量浓度小于 60 mg/L (平衡质量浓度 < 2 mg/L) 时, 胡敏酸对 Cd²⁺ 的吸附量随着 Cd²⁺ 质量浓度的增加快速增大; 之后, 胡敏酸对 Cd²⁺ 的吸附量小幅度增加至趋于稳定. 由于羧基的酸度系数 (pK_a) = 3, 当 pH = 5.0 时, 胡敏酸中 [COO⁻]/[COOH] 的比值为 100 : 1, 大部分羧基官能团可用于

Cd²⁺ 的吸附. 当 Cd²⁺ 质量浓度低时, 阳离子结合点充足, 能够有效吸附 Cd²⁺; 随着 Cd²⁺ 质量浓度增加, 羧基被阳离子饱和, 达到饱和吸附量^[31].

图 6 胡敏酸对 Cd²⁺ 的吸附等温线Fig.6 Isotherm of Cd²⁺ adsorption by leonardite-derived humic acid

对试验数据采用 Langmuir 和 Freundlich 吸附模型进行拟合分析. Langmuir 模型是表层单分子吸附, 吸附过程在吸附材料表面进行且表面吸附能量均匀; Freundlich 模型是一个经验模型, 描述了吸附体系是复杂的, 吸附过程不仅仅发生单分子层吸附.

Langmuir 方程:

$$Q = Q_m \cdot K_L \cdot C_e / (1 + K_L \cdot C_e) \quad (1)$$

Freundlich 方程:

$$Q = K_F \cdot C_e^{1/n} \quad (2)$$

其中: Q 为吸附平衡时的吸附量, mg/g; Q_m 为用 Langmuir 方程计算吸附饱和时的最大吸附量, mg/g; C_e 为吸附平衡时金属离子质量浓度, mg/L; K_L 为 Langmuir 常数, L/mg, 表征吸附能力; K_F 和 1/n 是 Freundlich 常数, 分别表征亲和系数和吸附强度. 拟合结果表明, Langmuir 模型能更好地描述胡敏酸对 Cd²⁺ 的吸附行为 (表 2), 胡敏酸对 Cd²⁺ 的吸附更符合单分子层吸附. 经过 Langmuir 方程计算, 在本试验条件下胡敏酸对 Cd²⁺ 的饱和吸附量达 137.37 mg/g. 与文献报道的饱和吸附量 (表 3) 进行比较发现, 从新疆风化煤提取的胡敏酸对 Cd²⁺ 的饱和吸附量远高于表 3 中其他研究者所用的从煤炭和土壤提取的胡敏酸对 Cd²⁺ 的饱和吸附量. 从新疆风化煤提取的胡敏酸对 Cd²⁺ 有较高的吸附量, 可能与其较高的官能团含量有关, 其羧基质量摩尔浓度高达 5.81 mol/kg (表 1). 在 pH = 5.0 时的饱

和吸附量(137.37 mg/g)只相当于占用了胡敏酸中71%的羧基.从新疆风化煤提取的胡敏酸对

Cd^{2+} 的饱和吸附量也高于赤泥^[32]、杉叶^[33]、劣质煤^[34]对 Cd^{2+} 的吸附量.

表2 胡敏酸吸附 Cd^{2+} 的Langmuir和Freundlich模型拟合参数

Table 2 Parameters of Langmuir and Freundlich models for Cd^{2+} adsorption by leonardite-derived humic acid

Freundlich 模型 Freundlich model			Langmuir 模型 Langmuir model		
1/n	K_F	R^2	$Q_m/(\text{mg/g})$	$K_L/(\text{L/mg})$	R^2
0.203	75.25	0.891	137.37	3.83	0.991

Q_m :最大吸附量. Q_m : Maximum adsorption capacity.

表3 胡敏酸对 Cd^{2+} 的吸附效果对比

Table 3 Comparison of Cd^{2+} adsorption capacities of humic acid from this study and in literature

材料 Materials	文献 References	来源 Source	$\rho(\text{Cd}^{2+})/(\text{mg/L})$	pH	$Q_m/(\text{mg/g})$
胡敏酸 HA	本研究 Present study	风化煤 Leo	0~100	5.0	137.37
胡敏酸 HA	[35]	腐殖土 Humus	0~224	5.5	100.18
胡敏酸 HA	[22]	煤炭 Coal	28~562	1~4	62.94
胡敏酸 HA	[36]	土壤 Soil	0~11 200	5.5±0.1	70.81

Q_m :最大吸附量. Q_m : Maximum adsorption capacity; HA: Humic acid; Leo: Leonardite.

2.2.4 风化煤提取的胡敏酸与IHSS标样吸附量的比较

在 $\text{pH}=4.3$ 、 Cd^{2+} 初始质量浓度为80 mg/L的相同试验条件下,风化煤提取的胡敏酸和IHSS标样1R106H对镉的吸附量分别是86.97和73.49 mg/g.虽然前者的COOH含量略小(表1),但其吸附量反而较大,这可能是因为1R106H标样在吸附试验过程中已经有少量溶解,部分与羧基络合的 Cd^{2+} 存在于溶液中,导致测得的吸附量较低.这从另一个方面显示出新疆风化煤提取的胡敏酸的一个实用优点,即在酸性条件下比较稳定,在 $\text{pH}<6.0$ 时基本不溶解,用于酸性土壤不太会造成 Cd^{2+} 和胡敏酸形成可溶态复合物随水迁移.这也正是农田重金属钝化/稳定化技术的基础.

3 讨论

风化煤俗称露头煤,是接近于地表的烟煤、褐煤、无烟煤等经过空气、阳光、雨雪等自然条件风化作用形成的产物.它含氧量高、热值低,不适合作为燃料使用.但新疆昌吉产的风化煤腐殖质丰富,是提取胡敏酸的优质原料,且储量大、价格低;提取的胡敏酸含很高的羧基(5.81 mol/kg),对 Cd^{2+} 的吸附量随 Cd^{2+} 质量浓度和 pH 升高而增加,在 $\text{pH}=6.0$ 时最高.在酸

性($\text{pH}=5.0$)及1 mmol/L NaNO_3 共存(模拟湿润地区酸性土壤溶液的离子强度)条件下对 Cd^{2+} 的饱和吸附量仍高达137.37 mg/g.这对于开发该风化煤在酸性重金属污染土壤修复中的应用至关重要.

目前,我国南方农田重金属污染严重,带来食品安全和人体健康方面的担忧^[10-11].重金属污染土壤的修复方法有很多,钝化/稳定化技术具备操作简单、不破坏土壤结构、不影响农业生产等优点,有望成为修复重金属污染农田的重要技术之一.在钝化技术中,修复材料的选择是难点之一.胡敏酸具备环境友好、价格适中、在土壤中保留时间较长、吸附量大等优点,倍受重视.从新疆风化煤提取的胡敏酸对 Cd^{2+} 具有很强的吸附能力,且风化煤本身(Cd、Pb、Cu、Zn分别为0.15、2.81、6.51、69.56 mg/kg)及提取的胡敏酸(Cd、Pb、Cu、Zn分别为0.15、3.23、6.09、19.57 mg/kg)重金属含量都不高,符合现有土壤环境质量标准.因此,它们有望在修复重金属污染土壤方面得到实际应用.

我国南方农田以酸性土壤($\text{pH}=4.5\sim 6.0$)为主,普遍具有土壤养分有效性低、矿质养分流失严重的问题,重金属在酸性土壤中活性高,易被作物吸收,添加胡敏酸可提供离子交换和络合作用以降低土壤溶液中的 Cd^{2+} 浓度^[37],减少作物吸收.当土壤 pH 接近于中性时,少量胡敏酸会溶解,可带着 Cd^{2+}

随渗滤液向下移动.但酸性土壤底土通常都有铁-铝-锰(水合)氧化物,易与胡敏酸和 Cd^{2+} 形成稳定的矿物-有机质-Cd 复合体^[38],从而被截留在底土.因此,胡敏酸既有钝化表土的 Cd^{2+} 、减少作物吸收的功效,又有带着表土中的 Cd^{2+} 向下移动、固定在底土的潜能,在治理酸性土壤重金属污染方面具有一定潜力,值得进行小规模田间试验.此外,胡敏酸还能改善土壤物理、化学及生物学性质,不会像施用石灰那样造成有机质分解和土壤板结,且胡敏酸的田间施用过程比较安全,不会灼伤操作人员.

4 结论

从新疆风化煤中提取的胡敏酸含量高达 90% (含 7.87% 灰分).与风化煤相比,提取的胡敏酸的 C、-COOH 含量增大,灰分含量明显降低.风化煤和胡敏酸的等电点分别是 4.3 和 2.7.胡敏酸对 Cd^{2+} 的吸附在 8 h 时达到平衡;pH 明显影响胡敏酸对 Cd^{2+} 的吸附,当 pH=6.0 时胡敏酸对 Cd^{2+} 的吸附量最大;在 pH=5.0、 Cd^{2+} 的初始质量浓度为 0~100 mg/L 时,胡敏酸对 Cd^{2+} 的饱和吸附量达 137.37 mg/g,比已有的相关文献报道的吸附量高,这和本文所用胡敏酸羧基含量较高有关.在相同试验条件下, Cd^{2+} 初始质量浓度为 80 mg/L 时,胡敏酸对 Cd^{2+} 的吸附能力 (86.97 mg/g) 高于 IHSS 标样 1R106H (73.49 mg/g).由于风化煤来源广、储量大、价格低,制备获得的胡敏酸产量高、吸附能力强、环境友好,胡敏酸有望作为吸附剂用于含重金属废水处理,作为钝化剂和土壤调理剂用于重金属污染土壤的修复.

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