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蛋氨酸改性类水滑石对水中 As(III)/As(V)  
的吸附过程及机理研究

Study on As(III)/As(V) Adsorption Process and Mechanisms of  
Met Modified LDHs in Water

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## 目录

目录.....	i
Contents .....	v
摘要.....	I
Abstract .....	III
<b>第一章 绪论</b> .....	<b>1</b>
1.1 砷简介.....	1
1.1.1 砷的基本性质.....	1
1.1.2 砷的来源和危害.....	2
1.1.3 水中砷的存在形态.....	3
1.2 水中砷的去除技术.....	4
1.2.1 混凝法.....	4
1.2.2 沉淀法.....	5
1.2.3 膜分离法.....	5
1.2.4 离子交换法.....	6
1.2.5 生物法.....	7
1.2.6 吸附法.....	7
1.3 类水滑石除砷进展.....	9
1.3.1 类水滑石的结构、性质和制备.....	9
1.3.2 类水滑石在砷吸附过程中的应用和机理研究.....	11
1.3.3 氨基酸改性插层类水滑石除砷进展.....	12
1.4 研究目标与研究内容.....	13
<b>第二章 材料与方 法</b> .....	<b>15</b>
2.1 试剂和材料.....	15
2.2 仪器和设备.....	16
2.3 测定方法.....	17

2.3.1 砷含量的检测.....	17
2.3.2 磷含量的检测.....	19
2.4 氨基酸插层类水滑石的制备.....	20
2.5 吸附性能评价.....	22
2.5.1 吸附剂量的影响.....	22
2.5.2 pH 及离子强度的影响.....	22
2.5.3 吸附动力学.....	22
2.5.4 吸附等温线.....	23
2.5.5 共存离子的影响.....	23
2.5.6 解吸附.....	23
2.6 吸附过程中的表征.....	24
2.6.1 X 射线粉末衍射.....	24
2.6.2 元素分析.....	24
2.6.3 热重分析.....	24
2.6.4 低温 N <sub>2</sub> 物理吸附.....	25
2.6.5 扫描电镜.....	25
2.6.6 傅里叶变换红外光谱.....	25
2.6.7 X 射线光电子能谱.....	26
2.6.8 电感耦合等离子发射光谱.....	26
2.6.9 核磁共振.....	26
<b>第三章 蛋氨酸改性 LDHs 对 As(III)的吸附过程与机理研究 .....</b>	<b>27</b>
3.1 引言.....	27
3.2 氨基酸插层 LDHs 制备条件的优化.....	27
3.2.1 有机插层化合物的筛选.....	27
3.2.2 合成 pH 值的影响.....	28
3.2.3 合成温度的影响.....	29
3.2.4 晶化温度的影响.....	30
3.2.5 晶化时间的影响.....	30
3.3 蛋氨酸改性插层锌铝类水滑石 (Zn <sub>2</sub> Al-Met-LDHs) 的表征.....	31

3.3.1 XRD 表征 .....	31
3.3.2 热性能分析.....	33
3.3.3 比表面积和粒径分析.....	33
3.3.4 元素分析及结构通式的确定.....	35
3.4 As(III)吸附性能评价 .....	36
3.4.1 吸附剂量的影响.....	36
3.4.2 pH 及离子强度的影响.....	37
3.4.3 吸附动力学.....	38
3.4.4 吸附等温线.....	40
3.5 Zn <sub>2</sub> Al-Met-LDHs 吸附 As(III)的机理分析.....	42
3.5.1 SEM 分析 .....	42
3.5.2 FTIR 分析.....	43
3.5.3 XPS 分析 .....	45
3.5.4 核磁共振.....	50
3.5.5 吸附机理.....	54
3.6 共存离子对 As(III)吸附的影响 .....	54
3.6.1 共存阴离子的影响.....	54
3.6.2 共存阳离子的影响.....	56
3.6.3 As(III)/P 共存的影响 .....	56
3.6.4 解吸附.....	58
3.7 本章小结.....	58
<b>第四章 蛋氨酸改性 LDHs 对 As(V)吸附及影响因素研究 .....</b>	<b>60</b>
4.1 引言.....	60
4.2 As(V)吸附性能评价.....	60
4.2.1 吸附剂量的影响.....	60
4.2.2 pH 及离子强度的影响.....	61
4.2.3 吸附动力学.....	63
4.2.4 吸附等温线.....	64
4.3 Zn <sub>2</sub> Al-Met-LDHs 对 As(V)吸附机理分析.....	66

---

4.3.1 FTIR.....	66
4.3.2 XPS .....	67
4.3.3 吸附机理.....	70
4.4 共存离子对 As(V)吸附的影响.....	71
4.4.1 共存阴离子的影响.....	71
4.4.2 共存阳离子的影响.....	72
4.4.3 As(V)/P 共存的影响 .....	73
4.4.4 解吸附.....	74
4.5 本章小结.....	75
<b>第五章 结论与建议 .....</b>	<b>77</b>
5.1 结论.....	77
5.2 创新点.....	79
5.3 建议.....	79
参考文献.....	80
在学期间科研成果 .....	91
致谢.....	92

## Contents

Contents in Chinese .....	i
Contents in English.....	v
Abstract in Chinese.....	I
Abstract in English.....	III
Chapter 1 Introduction .....	1
1.1 Introduction of arsenic .....	1
1.1.1 Basic properties of arsenic .....	1
1.1.2 The source and harm of arsenic .....	2
1.1.3 The form of arsenic in water .....	3
1.2 Arsenic removal technology .....	4
1.2.1 Coagulation .....	4
1.2.2 Precipitation .....	5
1.2.3 Membrane separation.....	5
1.2.4 Ion exchange .....	6
1.2.5 Biological method .....	7
1.2.6 Adsorption method.....	7
1.3 The research process of arsenic adsorption by hydrotalcite .....	9
1.3.1 The structure, properties and preparation of hydrotalcite .....	9
1.3.2 The application and mechanism analysis of hydrotalcite in arsenic adsorption.....	11
1.3.3 The research of Met modified hydrotalcite in arsenic adsorption .....	12
1.4 The objects and contents of the research .....	13
Chapter 2 Materials and methods .....	15
2.1 Experiments reagents and materials.....	15
2.2 Experiment instruments and equipments .....	16



2.3 Determination methods .....	17
2.3.1 Determination of arsenic .....	17
2.3.2 Determination of phosphorus .....	19
2.4 Preparation of hydrotalcite by amino acid modified .....	20
2.5 Adsorption performance of absorbents .....	22
2.5.1 The effects of adsorption dose .....	22
2.5.2 The effects of pH and ion strength .....	22
2.5.3 Adsorption kinetics study .....	22
2.5.4 Adsorption isotherm study .....	23
2.5.5 The effects of coexisting ions .....	23
2.5.6 Desorption study .....	23
2.6 Characterization of materials .....	24
2.6.1 X-ray diffraction .....	24
2.6.2 Thermogravimetric analysis .....	24
2.6.3 TG/DTG .....	24
2.6.4 Nitrogen adsorption .....	25
2.6.5 Scanning electron microscope .....	25
2.6.6 Fourier transform infrared spectrometer .....	25
2.6.7 X-ray photoelectron spectroscopy .....	26
2.6.8 Inductively coupled plasma optical emission spectrometer .....	26
2.6.9 Nuclear magnetic resonance .....	26
Chapter 3 Adsorption process and mechanisms study of As(III) by Met modified Zn <sub>2</sub> Al-LDHs .....	27
3.1 Introduction .....	27
3.2 Optimization of preparation conditions by amino acid modified LDHs .....	27
3.2.1 Influence of intercalation compounds .....	27
3.2.2 Influence of preparation pH .....	28
3.2.3 Influence of preparation temperature .....	29

3.2.4 Influence of aging temperature .....	30
3.2.5 Influence of aging time .....	30
3.3 Characterization of Zn <sub>2</sub> Al-Met-LDHs .....	31
3.3.1 X-ray diffraction .....	31
3.3.2 TG/DTG .....	33
3.3.3 Nitrogen adsorption .....	33
3.3.4 Composition analysis and general formula confirmtion .....	35
3.4 Adsorption performance analysis of As(III) .....	36
3.4.1 Influence of absorbent dose .....	36
3.4.2 Influence of pH and ion strength .....	37
3.4.3 Adsorption kinetics study .....	38
3.4.4 Adsorption isotherm study .....	40
3.5 Adsorption mechanism analysis of As(III) .....	43
3.5.1 SEM analysis .....	43
3.5.2 FTIR analysis .....	43
3.5.3 XPS analysis .....	45
3.5.4 NMR analysis .....	50
3.5.5 Mechanisms analysis .....	54
3.6 Influence of coexisting ions on As(III) adsorption .....	54
3.6.1 Influence of coexisting anions .....	54
3.6.2 Influence of coexisting cations .....	56
3.6.3 Influence of As(III)/P competition adsorption .....	56
3.6.4 Desorption .....	58
3.7 Summary .....	58
 Chapter 4 Adsorption process and influence study of As(V) by Met modified LDHs .....	 60
4.1 Introduction .....	60
4.2 Adsorption performance analysis of As(V) .....	60

4.2.1 Influence of absorbent dose .....	60
4.2.2 Influence of pH and ion strength .....	61
4.2.3 Adsorption kinetics study.....	63
4.2.4 Adsorption isotherm study .....	64
4.3 Adsorption mechanism analysis of As(V) .....	66
4.3.1 FTIR analysis .....	66
4.3.2 XPS analysis .....	67
4.3.3 Mechanisms analysis .....	70
4.4 Influence of coexisting ions on As(V) adsorption .....	71
4.4.1 Influence of coexisting anions .....	71
4.4.2 Influence of coexisting cations .....	72
4.4.3 Influence of As(V)/P competition adsorption .....	73
4.4.4 Desorption.....	74
4.5 Summary .....	75
<b>Chapter 5 Conclusions and suggestions .....</b>	<b>77</b>
5.1 Conclusions.....	77
5.2 Highlights.....	79
5.3 Suggestions .....	79
<b>References.....</b>	<b>80</b>
<b>Publications.....</b>	<b>91</b>
<b>Acknowledgements.....</b>	<b>92</b>

## 摘要

砷是一种高毒性的类金属元素,目前由于人们日常生活中使用的添加剂和矿产开发等,造成了大量的环境水体砷污染,严重威胁着人们的饮水安全。因此,开发合适的材料对水中砷进行去除是当前含砷废水资源化应用和饮用水安全的关键。基于生物体内巯基蛋白质和砷的甲基化解毒作用机理,本论文通过恒定pH法对锌铝类水滑石(Layered Double Hydroxides, LDHs)进行改性,合成含有硫的蛋氨酸(Met)插层LDHs。结合宏观吸附动力学、等温线、共存离子的影响和反应前后材料的微观表征,分别研究了有机物改性前后的类水滑石对As(III)和As(V)的吸附过程和机理,探讨含硫氨基酸在体外与砷的结合机制。研究结果表明:

(1) 通过共沉淀法合成的蛋氨酸改性类水滑石( $Zn_{0.7}Al_{0.3}(OH)_2$  (Met) $_{0.3} \cdot 0.32H_2O$ )具有良好的晶体结构且热力学稳定。其在水中对As(III)具有较好的吸附性能,在298 K、318 K、338 K时对As(III)的最大理论吸附容量分别为94.11 mg/g, 108.44 mg/g, 88.39 mg/g, 远高于一般的除砷材料。动力学和吸附等温线表明As(III)的吸附是一个吸热、有利的反应,在一定范围内,温度升高,有利于反应的进行。

(2) 通过FTIR、XPS、NMR机理分析表明,羧基和硫的存在可大大促进As(III)的吸附,且硫的作用明显大于羧基的作用。在As(III)反应过程中, Met上的-C=O键中O原子可与 $H_3AsO_3$ 中的-OH形成氢键,其中-OH作为氢键的供体, -C=O中的O原子为氢键的受体,从而促进As(III)的去除。另外,蛋氨酸中含有的硫由于其原子外围含有孤对电子,易与 $As^{3+}$ 形成环状的络合物,从而提高对As(III)的去除。

(3)  $Zn_2Al$ -Met-LDHs对As(V)的吸附也是一个快速的、吸热反应,且较好的符合拟二级动力学模型,升高温度有利于反应的进行;298 K和338 K时,Langmuir能较好的拟合As(V)的吸附等温线,当温度升高到318 K时,Freundlich更能较好拟合As(V)的吸附,其最大理论吸附容量分别为77.82 mg/g, 90.90 mg/g, 77.52 mg/g。FTIR和XPS表征分析表明, $Zn_2Al$ -Met-LDHs对As(V)的吸

附一方面通过表面金属的静电作用、离子交换等非特异性吸附去除；另一方面则是通过插层蛋氨酸根离子与 As(V)发生化学反应去除，如氢键等。

(4) 在阴阳共存离子影响时，砷的吸附受磷的影响较大，随 P 浓度的增大，As(V)吸附容量明显减小，而 As(III)变化却较小；且当溶液中含有金属阳离子存在时，可明显提高 As(V)吸附容量。在不同解析液中，As(V)的解析量由水中的 3.8%分别增加到 39.1%、22.9%、14.9% (NaOH、Na<sub>2</sub>CO<sub>3</sub>、Na<sub>2</sub>HPO<sub>4</sub>)。而 As(III)则不容易解析下来，在不同的解析液中，其解析量分别为 5.3%、8.7%、7.4%、6.4%。

本文通过有机物蛋氨酸插层 LDHs 的改性，制备了对砷具有高去除率的 Zn<sub>2</sub>Al-Met-LDHs。并详细探讨了砷的吸附过程与机理，同时探讨了水中共存离子对砷吸附性能的影响，为高效、经济的除砷吸附剂改性、制备和利用提供一定的借鉴。

**关键字：**插层 LDHs；砷；吸附；蛋氨酸

## Abstract

Arsenic is a highly toxic metalloid element, arsenic pollutions are more and more serious in water because of the additives used in daily life and the mineral development and so on. It may seriously affect people's drinking water safety. Therefore, developing appropriate materials to remove arsenic in water is the key to wastewater recycle and the safety of drinking water. In this paper the zinc/aluminum hydrotalcite (Layered Double Hydroxides, LDHs) was synthesized by coprecipitation method and methionine(Met) was intercalated LDHs. Batch experiments and microscopical analysis are used to investigate the adsorption performances and mechanisms for arsenite and arsenate removal. The combination of sulfur-containing amino acids and arsenic in vitro were discussed. The main results are shown as follows.

(1) Methionine acid (Met) intercalated  $Zn_2Al$  layered double hydroxides ( $Zn_{0.7}Al_{0.3}(OH)_2 (Met)_{0.3} 0.32H_2O$ , denoted as  $Zn_2Al$ -Met-LDHs) were successfully prepared by coprecipitation method. The synthetic materials had a good crystal structure and were good at thermal stability. The maximum adsorption capacity were 94.11 mg/L, 108.44 mg/L and 88.39 mg/L in 298 K, 318 K, 338 K, which were higher than that of any other reported materials. In addition, adsorption kinetics and isotherms were shown that the temperature increased at a range would be better for the arsenite adsorption.

(2) The FTIR, XPS and NMR characteristic analysis verify that the high adsorption capacity is attributed to the hydrogen bond and  $-S-CH_3$ . In the adsorption process, there existed a hydrogen bond between the  $-OH$  of  $H_3AsO_3$  and the O of  $C=O$ . The  $-OH$  is the donor and combines with the acceptor of carboxyl group by electronic transform. In addition, the  $-S-$  also enhanced adsorption by chelation because of the character of sulphur atom.

(3) Pseudo-second-order was suitable for the arsenate adsorption process by  $Zn_2Al$ -Met-LDHs. Meanwhile the adsorption was a fast and endothermic reaction.

The adsorption capacity increased with the temperature from 298 K to 338 K, and Langmuir could fit well than the other models. While the Freundlich model could fitted well when the temperature reached 318 K. The maximum adsorption capacity are 77.82 mg/g, 90.90 mg/g and 77.52 mg/g respectively. FTIR and XPS suggested that the adsorption of arsenate by Zn<sub>2</sub>Al-Met-LDHs not only be removed by the surface electrostatic interaction and ion exchange, but also could be a chemical reaction between adsorbent and adsorbate, such as hydrogen bond.

(4) The arsenic adsorption capacity changed with the molar concentration of phosphate in water when considering coexisting ions effects. With the ratio of phosphate increased, the capacity of arsenate decreased more significantly than arsenite. Meanwhile the capacity of arsenate increased with the addition of cations. In the desorption experiments, the desorption rate of arsenate increased from 3.8% to 39.0%, 22.9%, 14.9% in different desorption solutions H<sub>2</sub>O, NaOH, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>HPO<sub>4</sub>. However the arsenite couldn't be desorpted easily, the desorption rate were only 5.3%, 8.7%, 7.4% and 6.4% in different desorption solutions.

This study prepared an organic intercalated Zn<sub>2</sub>Al-Met-LDHs, which processed a high capacity towards arsenite and arsenate. In addition, their adsorption behaviors and mechanisms were studied in detail. This work not only presented a well performed material for arsenic removal but also useful materials for further researches on adsorbents modified, prepared and reuse about arsenic removal.

**Keywords:** Intercalated LDHs; Arsenic; Adsorption; Methionine acid

## 第一章 绪论

随着现代科技进步,人们在追求快速发展的同时也越来越注重环境问题。研究发现,在我国乃至世界很多国家,水体环境污染已严重威胁着人们的身体健康。其中,最为突出的就包括水中砷污染。水中砷污染会引起慢性中毒,这种隐蔽的毒性往往比急性砷中毒危害更大<sup>[1]</sup>。在我国,水中砷污染主要表现在地下水污染和工业含砷废水污染两方面。调查发现,在新疆、湖南、山西等地区,地下水砷浓度调查显示也高达 1000  $\mu\text{g/L}$  以上,远远高于我国饮用水含砷标准。而这些地区饮用水大部分来源于地下水,无疑造成了严重的水体砷慢性中毒事件<sup>[2]</sup>。另外,工业砷污染主要包括矿石的冶炼、某些化学物质的提炼等,这部分砷污染主要是人为作用。2008 年以来,我国就先后报道了贵州、湖南、河池、云南、广西等地都有砷污染事件发生,且近几年随着经济技术的发展,水中砷污染呈现爆发趋势<sup>[3]</sup>。特别是在人口密集地区的湖泊、水库等都有不同程度的砷污染,严重威胁着人体饮用水安全。一般,在人体内,砷的代谢主要是通过巯基蛋白的甲基化,将无机砷转化成有机砷<sup>[4, 5]</sup>。而在体外砷的甲基化和含硫有机物与砷的结合研究则较少。因此,本研究主要通过含硫的氨基酸改性类水滑石材料,探讨体外氨基酸与砷的去除机理。

### 1.1 砷简介

#### 1.1.1 砷的基本性质

砷(Arsenic)是元素周期表中第四周期第 VA 主族,具有典型的金属和非金属元素性质,属于过渡元素的一种。砷的原子序数为 33,相对原子质量为 74.92<sup>[6]</sup>。通常砷具有黄、灰、黑褐三种同素异形体,其中灰色的晶体具有金属的性质,脆而硬,密度为 5.727  $\text{kg/L}$ ,熔点为 817  $^{\circ}\text{C}$ ,具有+3 和+5 两种价态<sup>[7]</sup>,加热时可与大多数金属和非金属发生反应。常温下不溶于水,相对比较稳定。但易溶于硝酸和王水,也能溶于强碱,生成砷酸盐。

自然界中极少有单质砷的存在,虽然砷在地壳中的总体含量不大,但是它在自然界中却无所不在<sup>[8]</sup>。通常在岩石中砷的含量约为 0.5~2.5  $\text{mg/kg}$ ,略低于沉积物和磷钙土中,总含量分布排在第 20 位;而海水中砷的含量排在第 14 位,平均



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