

# 氧化铁涂层砂变性滤料除砷性能研究

## Study on Performance for Arsenic Removal by Iron-Oxide-Coated Filter Media

高乃云 徐迪民 范瑾初 (同济大学污染控制与资源化研究国家重点实验室, 上海 200092)

Gao Naiyun Xu Dimin Fan Jinchu (State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092)

**摘要** 氧化铁涂层砂和未涂层石英砂除砷过滤实验比较表明, 氧化铁涂层砂除砷效果显著, 去除率达95%以上, 基本遵循低pH, 高去除率的规律; 除砷吸附等温线属于Langmuir型, 单层吸附。

**关键词:** 氧化铁涂层砂 除砷 改性滤料 石英砂



**作者简介:** 高乃云, 1950年生, 1974年毕业于同济大学给排水工程专业, 博士, 教授。长期从事给水处理、给水管网和建筑给排水方面的教学、科研和工程设计项目。参加的“黄浦江污染综合治理规划方案研究”子课题“生物滤塔研究”获国家环保局环保科技进步一等奖, “上海市城市供水优化方案研究”获1992年上海市科技进步一等奖等。参加《环境工程手册》(水污染防治卷)和《给水排水工程快速设计手册》的部分编写工作。在《中国给水排水》和《给水排水》等杂志发表文章数篇。

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### 1 氧化铁涂层砂(简称涂铁砂)的制备及表面特性

#### 1.1 氧化铁涂层砂变性滤料的制备

将200g在高温条件下制备好的涂 $\text{FeCl}_3$ 砂置入100mL 2.5mol/L三氯化铁溶液中混合, 在110℃烘箱中烘干, 在空气中冷却, 冷却后的涂层因吸水而变得很潮湿, 然后再烘干, 待涂层稳定, 用蒸馏水冲洗干净, 烘干待用。

#### 1.2 涂铁砂的比表面积

同济大学玻尔物理实验室采用BET法测得原砂与涂铁砂的比表面积, 见表1。结果表明, 涂铁砂的比表面

表1 比表面积测试结果

Table 1 Test results of specific surface areas

测试滤料	取样量(g)	总表面积( $\text{m}^2$ )	比表面积( $\text{m}^2/\text{g}$ )
石英砂	3.664	0.83	0.227
涂铁砂	3.185	9.65	3.03

积比石英砂大大增加, 是原砂的13.35倍。

#### 1.3 采用X射线衍射鉴定涂铁砂表面

经复旦大学测试中心的X射线衍射鉴定分析, 涂铁砂表面主要是赤铁矿( $\text{Fe}_2\text{O}_3$ )。其X射线衍射图的峰与复旦大学物质标准数据集33-0664号卡片的相应峰吻合。

#### 1.4 涂铁砂的扫描电子显微镜表面分析

从扫描电子显微镜照片中可明显地看出,  $\text{FeCl}_3$ 水解聚合物覆盖和沉积于石英砂表面, 聚合物排列整齐均匀。

## 2 试验装置与试验方法

试验装置采用泵式系统, 流程为:

原水装置→蠕动泵→滤柱→出水

分别将涂铁砂和石英砂装入滤料, 高度为40cm的2个滤柱中, 做动态平行对比过滤实验。

## 3 涂铁砂除砷效果

#### 3.1 涂铁砂与石英砂的除砷效果

过滤试验中, 初始滤速采用4.89m/h, 原水含砷浓度10.25mg/L, 过滤时间3h, 结果见表2。

表2 涂铁砂和石英砂除砷效果比较

Table 2 Comparison effects of arsenic removal by IOCS with quartz sand

过滤时间(h)	As去除率(%)	
	石英砂	涂铁砂
1	2.49	100
2	0	99.52
3	0	100

#### 3.2 除砷的影响因素

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## 3.2.1 砷的去除率与 pH 的关系

涂铁砂除砷过滤中,砷的去除率随 pH 的变化见图 1。由图 1 可见,低 pH 值有利于砷去除。即去除率随 pH 的增大而从 100%去除率开始缓慢降低。

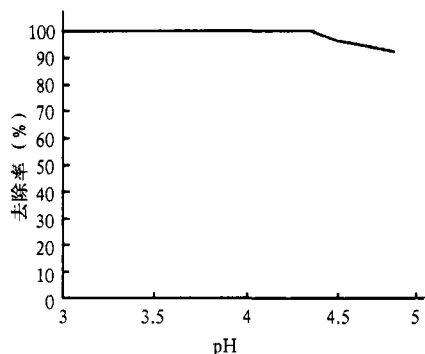


图 1 砷去除率与 pH 的关系

Figure 1 Effect of pH levels on arsenic removal

## 3.2.2 As 去除率与过滤时间的关系

原水含 As 浓度为 10.25mg/L, 滤速为 4.89m/h, 过滤过程中, As 去除率 6h 后, 随过滤时间的延长而下降, 见图 2。

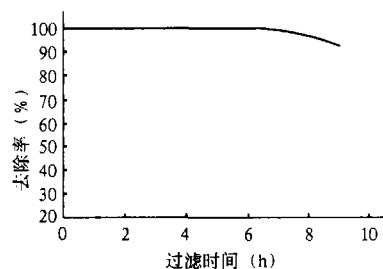


图 2 As 去除率与过滤时间的关系

Figure 2 Removal of arsenic versus filtration time

## 4 涂铁砂除砷吸附等温线

## 4.1 涂铁砂除砷吸附等温线实验

在 6 只锥形烧瓶中各加入涂铁砂 5g, NaCl 10mL 以增强离子强度, 分别加入含砷原水至 100mL, 含砷浓度分别为 102.5、205.0、307.5、410.0、615.0、820.0mg/L。在 28℃ 条件下, 以 100r/min 速度震荡 24h, 期间 3 次用 NaOH 和 HCl 调整 pH, 使其始终接近 7.0。然后用 0.45 μm 孔径滤膜过滤上清液, 稀释 50 倍, 测定各平衡浓度。利用式(1)计算吸附容量等, 结果见表 3; 绘制吸

表 3 除砷吸附等温线试验数据计算表

Table 3 Calculating test data of adsorption isotherm for arsenic removal

水样 编号	初始浓度 $C_i$ (mmol/L)	平衡浓度 $C_e$ (mmol/L)	水样体积 $V$ (L)	涂铁砂重量 $m$ (g)	砷吸附容量 $q_e$ (mmol/g)	$C_e/q_e$ (g/L)
1	1.36813	0.105185	0.1	5	0.025259	4.164245
2	2.73625	0.576702	0.1	5	0.043191	13.35237
3	4.10437	1.628549	0.1	5	0.049517	32.88868
4	5.47250	2.898019	0.1	5	0.051490	56.28314
5	8.20876	5.509500	0.1	5	0.053985	102.0561
6	10.94501	8.084711	0.1	5	0.057206	141.3263

附等温线见图 3。

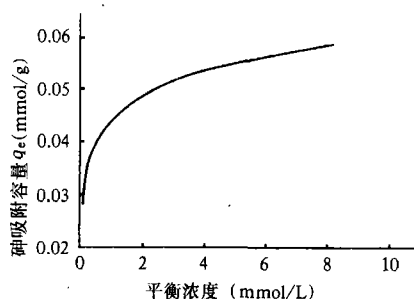


图 3 除砷吸附等温线

Figure 3 Adsorption isotherm of arsenic removal

$$q_e = x/m = [V(C_i - C_e)]/m \quad (1)$$

式中:

$x$ ——被吸附的物质(mmol);

$m$ ——吸附剂的质量(g);

$V$ ——水样的容积(L);

$C_i$ ——被吸附物的浓度(mmol/L);

$C_e$ ——吸附的平衡浓度(mmol/L);

$q_e$ ——吸附容量(mmol/g)。

图 3 所示的吸附等温线, 其形状与 Langmuir 型曲线<sup>[5]</sup>对比, 可初步判断其属于 I 型吸附等温线, 即 Langmuir 单分子层吸附。

## 4.2 除砷吸附公式的确定

Langmuir 吸附公式为:

$$q_e = x/m = b(q_e)^0 C_e / (1 + b C_e) \quad (2)$$

式中:

$b$ ——常数, 量纲为浓度;

$(q_e)^0$ ——吸附容量  $q_e$  的极限值;

用图解法<sup>[1,5]</sup>求  $b(q_e)^0$ 。用表 3 数据以  $C_e$  和  $C_e/q_e$  分别为横、纵坐标作图, 见图 4。

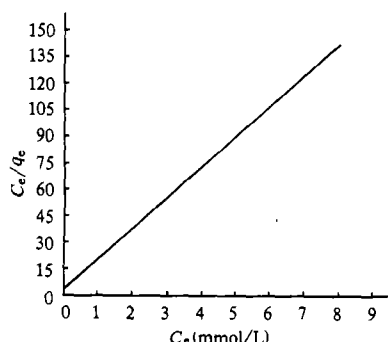


图4 求 Langmuir 公式的常数(除砷)

Figure 4 Solved constant for Langmuir equation of arsenic removal

通过对表3中的试验数据进行曲线拟合,得到图4中的直线方程为:

$$q_e = 17.279C_e + 4.1977$$

$$R^2 = 0.9985$$

由图中直线的截距及坡度可分别求得 $(q_e)^0$ 、 $b$ 值。

$$\begin{cases} 1/(q_e)^0 = 17.2790 \\ 1/b(q_e)^0 = 4.1977 \end{cases}$$

$$(q_e)^0 \approx 0.0579; b \approx 4.1144$$

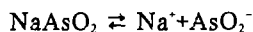
涂铁砂除砷的 Langmuir 吸附模型:

$$q_e = x/m = 0.2382C_e / (1 + 4.1144C_e) \quad (3)$$

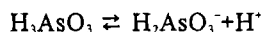
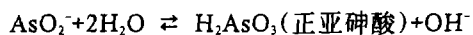
根据 Langmuir 理论<sup>[4]</sup>,被吸附的分子或离子有一定时间停留在活性中心上,然后又脱开吸附剂。已经被吸附的 $As^{3+}$ 或 $As^{5+}$ 还可以脱离固体表面,这就意味着存在一个平衡关系,当整个吸附表面上吸附的速度与解吸的速度相等时,吸附过程达到平衡。证明这种吸附是一种动态平衡过程。 $As$ 去除率与时间关系表明(3.2.2),活性中心完全被吸附物占据后,不再有吸附作用,因此,除砷是单分子层吸附。

## 5 除砷理论分析

本研究中原水用 $NaAsO_2$ 配制而成,其在水中离解为:



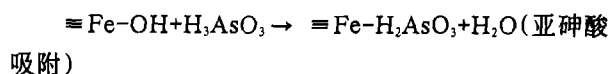
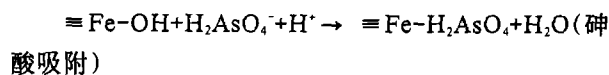
在酸性条件下,砷主要以以下形式存在:



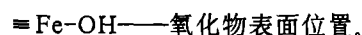
$H_2AsO_4^-$ 和 $H_3AsO_3$ 在水中占大多数。涂铁砂在等电点时的pH为8.5左右<sup>[2,3]</sup>。因此,在pH值=7的条件下,其表面带正电荷,而且比表面积是石英砂的13.5

倍,吸附容量远大于石英砂,有利于吸附带负电荷的 $AsO_2^-$ 、 $H_2AsO_4^-$ 、 $HAsO_4^{2-}$ 。

溶解的砷酸和涂铁砂的氧化物表面的吸附位置之间形成的表面络合物如下:



式中:



这些络合物被吸附,即覆盖于涂铁砂表面。当涂铁砂表面位置被占满,单分子层吸附饱和,除砷率显著下降。除砷过程中,实际上不是砷单独存在,而是许多种化合物共存的各种化合物在吸附时或是互相加强,或是互相阻碍,也有时彼此无关。原水中的pH值会影响砷的吸附,除了上述原因以外,pH值影响着砷化合物的电离状态,另一方面, $H^+$ 和 $OH^-$ 离子本身也可被强烈吸附,因而对其它物质吸附起影响作用。

## 6 结语

石英砂表面用氧化铁涂层,改变了石英砂的表面特性及带电性。使其在等电点时的pH,由0.7~2.2提高到8.5左右,在pH值<7的条件下,其表面带正电荷,有利于吸附水中带负电荷的 $AsO_2^-$ 、 $H_2AsO_4^-$ 、 $HAsO_4^{2-}$ 、中性分子、络合物等。同时涂层砂的比表面积是石英砂的13.5倍,吸附容量远大于石英砂。因此,氧化铁涂层砂除砷效果显著,去除率可达95%以上,基本遵循低pH,高去除率的规律;石英砂对水中的砷则有微量去除效果。经实验与验证表明,氧化铁涂层砂除砷吸附等温线属于Langmuir型,单层吸附。

## 7 参考文献

- 1 许保玖,安鼎年. 给水处理理论与设计. 中国建筑工业出版社,1992.
- 2 Jiban K Satpathy, Malay Chaudhuri. Treatment of cadmium-plating and chromium-plating by iron oxide-coated sand. Water Environ Research, 1995, 67(5): 788~790.
- 3 Mark M Benjamin et al. Sorption and filtration of metals using iron-oxide-coated sand, 1996, 30(11): 2609~2620.
- 4 尚仰震. 物理化学与胶体化学. 四川科学技术出版社,1986.
- 5 许保玖. 当代给水与废水处理原理讲义. 清华大学出版社,1983.

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**Characteristic Study of DNA Adduct  
8-Hydroxy-2-Deoxyguanosine**

Sun Yongmei Dai Shugui Xi Zhuge

(College of Environmental Science and Engineering,  
Nankai University, Tianjin 300071)

DNA adduct 8-hydroxy-2-deoxyguanosine (8-OH-dG) as a biomarker of oxidative DNA damage, its characteristic study is very important for realization of its stability, sensitivity, accuracy of quantitative determination as well as extensive investigation of the oxidative damage caused by the toxic materials *in vivo*. Studies on analysis, hydrolysis, storage and stability of 8-OH-dG in oxidatively damaged DNA have been conducted. The oxidative source, taking Fenton type reaction as a hydroxyl free radical generating system (such as chelator- $\text{Fe}^{2+}$ - $\text{H}_2\text{O}_2$  system), reacted with deoxyguanosine and calf thymus DNA to yield mounts of 8-OH-dG. 8-OH-dG was analyzed by HPLC-EC method, its sensitivity was 2-3 orders of magnitude higher than the spectrophotometric method, the detection limit was 3% fmol, and its dynamic range was 4 orders of magnitude, from 32pmol to 3.2 nmol, and correlation coefficient was 0.9996. Studies have also been conducted on enzymatic digestion conditions of DNA, storage pH, medium environment and stability etc. The results showed that there was less loss of 8-OH-dG stored in neutral and acidic buffer solution than in alkaline buffer solution and the amount of 8-OH-dG formed in DNA depending on the buffer system. The 8-OH-dG within DNA was accumulated under oxidative source or environment with oxygen, and improved that the method by adding antioxidants to detect 8-OH-dG in DNA were sensitive and accurate.

**Key words:** DNA adduct 8-OH-dG  
Environmental oxidants

**Transmission Electron Microscopic Observation  
on Morphology of Polyaluminum  
Silicate Chloride Flocculant**

Gao Baoyu Yue Qinyan

(School of Environmental Science and Engineering,  
Shandong University, Jinan 250100)

Wang Chunsheng

(School of Chemistry and Chemical Engineering,  
Shandong University Jinan 250100)

Morphology of polyaluminum silicate chloride  
(PASC) flocculant and polyaluminum chloride (PAC)

has been studied and compared by transmission electron microscope (TEM). Effect of basicity (B), Al/Si molar ratio and preparation procedure on morphology of PASC were also investigated. The experimental results showed that the size of PASC was larger than that of PAC. The size of PASC increased with increasing of B value and decreasing of Al/Si molar ratio. In comparison with PASC products prepared by composite technique, PASC products prepared by copolymerization technique were characterized by having bigger size.

**Key words:** Polyaluminum silicate chloride (PASC)  
Flocculant Morphology  
Transmission electron microscopic observation

**Study on Performance for Arsenic Removal by  
Iron-Oxide-Coated Filter Media**

Gao Naiyun Xu Dimin Fan Jinchu

(State Key Laboratory of Pollution Control and Resource  
Reuse, Tongji University, Shanghai 200092)

The performance of iron-oxide-coated sand (IOCS) and uncoated quartz sand in filtration for arsenic removal has been studied. IOCS removed arsenic from water reached the level of >95%, and the removal efficiency increased with decrease of pH value. The adsorption isotherm of arsenic removal belongs to Langmuir adsorption model and was valid for single-layer adsorption.

**Key words:** Iron-oxide-coated sand  
Arsenic removal  
Modified filter media  
Quartz sand

**Study on Synergetic Toxicity of Copper and  
Cadmium to Tadpole**

Yang Zaifu

(College of Life Science, East China Normal  
University, Shanghai 200062)

Synergetic toxicity of copper and cadmium to tadpole has been studied with acute tests. The result showed that  $\text{LC}_{50}$  of  $\text{Cu}^{2+}$  to tadpole were 0.201, 0.138 and 0.138 mg/L in 24h, 48h and 96h respectively.  $\text{LC}_{50}$  of  $\text{Cd}^{2+}$  to tadpole were 32.1, 23.3 and 18.9 mg/L in 24h, 48h and 96h respectively. The synergetic toxicity of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  to tadpole in 24h, 48h and 96h additive index were 1.03, 1.02 and 1.20 in 24h, 48h and 96h respectively.

**Key words:** Copper Cadmium Acute toxicity