

## 研究简报

玉米麸质铁去除废水中的  $\text{Cr(VI)}$ 

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**摘要** 本文研究了玉米麸质铁去除废水  $\text{Cr(VI)}$  过程中酸度、流速对去除率的影响以及再生和实验室放大试验等问题。结果表明,  $\text{Cr(VI)}$  去除率可达 99.9%, 动态饱和吸附量是  $27\text{mg/g}$ 。实验室放大试验结果满意。用  $0.3\text{mol} \cdot \text{L}^{-1} \text{NH}_3 \cdot \text{H}_2\text{O}$  可以再生。为小规模含铬废水的治理提供了一种价格便宜, 操作简单可靠的方法。

**关键词** 玉米麸质; 铬; 废水处理。

玉米麸质对金属阳离子有很好的吸附能力<sup>[1,2]</sup>, 可用于去除水中重金属阳离子。本文是将玉米麸质结合铁  $\text{Fe(III)}$  以后, 制成玉米麸质铁, 作为吸附材料去除废水中的  $\text{Cr(VI)}$  阴离子。实验表明, 玉米麸质铁对  $\text{Cr(VI)}$  有很好的吸附能力, 可以作为一种含  $\text{Cr(VI)}$  废水的处理材料。

## 一、材料和方法

玉米麸质是湿磨淀粉副产品, 经适当处理制成粒度为 30—80 目的麸质, 然后用  $\text{FeCl}_3$  溶液浸泡 24h 以上, 过滤、自然干燥、即成玉米麸质铁。堆密度  $0.7\text{g} \cdot \text{ml}^{-1}$ , 棕黄色硬质颗粒, 长时期水浸强度下降不多。有内孔结构。

含  $\text{Cr(VI)}$  试液用蒸馏水和  $\text{K}_2\text{Cr}_2\text{O}_7$  试剂配制, 使  $\text{Cr(VI)}$  浓度为  $100\mu\text{g} \cdot \text{ml}^{-1}$ 。六价铬的测定方法按 GB 7466-87 (高锰酸钾氧化-二苯碳酰二肼分光光度法) 进行。

小试柱子直径 10mm, 玉米麸质铁重 3.0g。实验室放大试验采用电镀车间废水, 柱子直径 8cm。去除率按下式计算,

$$\eta = (1 - c_i/c_0) \times 100\%$$

其中,  $\eta$  为去除率,  $c_i$  为出口水含  $\text{Cr(VI)}$  浓度,  $c_0$  为进口水含  $\text{Cr(VI)}$  浓度。

## 二、结果与讨论

1. 玉米麸质铁去除  $\text{Cr(VI)}$  的条件试验

(1) 试液酸度对去除率的影响 调节试液的 pH 值, 用 30ml 浓度为  $100\mu\text{g} \cdot \text{ml}^{-1}$  的  $\text{Cr(VI)}$  试液, 以  $5\text{ml} \cdot \text{min}^{-1}$  的流速过柱, 结果见表 1。

结果表明, 在  $\text{pH} = 2-10$  的范围内, 去除率都在 99.9%, 这表明麸质铁对  $\text{Cr(VI)}$  有很好的吸附能力。

(2) 过柱速率对去除率的影响 在其他条件相同的情况下, 以不同的过柱速率用浓度  $100\mu\text{g} \cdot \text{ml}^{-1}$  的  $\text{Cr(VI)}$  试液过柱, 测定

表 1 酸度对去除率的影响

pH	1.94	3.74	5.69	7.34	9.58
出水浓度 ( $\mu\text{g} \cdot \text{ml}^{-1}$ )	0.110	0.037	0.037	0.028	0.018
去除率 $\eta$	99.89	99.96	99.96	99.97	99.98

表 2 过柱速率对去除率的影响

过柱速率 ( $\text{ml} \cdot \text{min}^{-1}$ )	4.6	5.8	7.2	8.6	12.8	20.0	28.0
出水浓度 ( $\mu\text{g} \cdot \text{ml}^{-1}$ )	0.031	0.042	0.046	0.040	0.039	0.042	0.102
去除率 %	99.97	99.96	99.95	99.96	99.96	99.96	99.90

流出液中  $\text{Cr(VI)}$  的浓度,结果见表 2。

结果表明,在速率从  $5\text{ml} \cdot \text{min}^{-1}$  到  $28\text{ml} \cdot \text{min}^{-1}$  范围内,去除率都在 99.9% 以上。说明麸质铁对  $\text{Cr(VI)}$  的吸附能很快达到平衡。

(3) 动态吸附曲线 以含  $\text{Cr(VI)}$  浓度  $100\mu\text{g} \cdot \text{ml}^{-1}$  的试液连续过柱,流速  $5\text{ml} \cdot \text{min}^{-1}$ ,测定不同流过体积中  $\text{Cr(VI)}$  的浓度,结果如图 1。由动态吸附曲线看出,流过 320ml 后出口水  $\text{Cr(VI)}$  浓度不超过  $0.5\mu\text{g} \cdot \text{ml}^{-1}$ 。

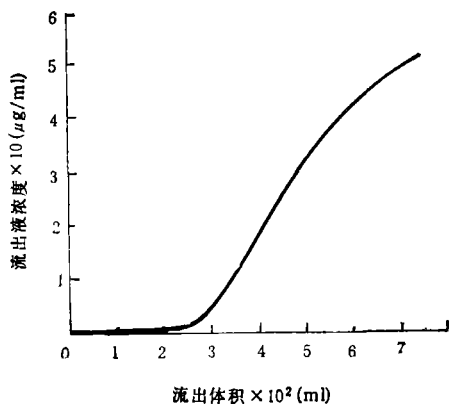


图 1 动态吸附曲线柱子直径  $\phi = 10\text{mm}$  吸附剂重 3.0g

(4) 动态饱和吸附量 在动态吸附试验中,当出口试液  $\text{Cr(VI)}$  浓度与进口试液  $\text{Cr(VI)}$  浓度相同时,计算出玉米麸质铁的动态饱和吸附量为  $27\text{mg} \cdot \text{g}^{-1}$  (以  $\text{Cr(VI)}$  计);而操作吸附量为  $10.6\text{mg} \cdot \text{g}^{-1}$ 。

2. 玉米麸质铁的再生及  $\text{Cr(VI)}$  的回收

(1) 洗脱曲线 用 2.5 倍柱体积的  $\text{NH}_3 \cdot \text{H}_2\text{O}$  ( $0.3\text{mol} \cdot \text{L}^{-1}$ ) 溶液浸 5min, 然后以

$2\text{ml} \cdot \text{min}^{-1}$  的速率放出。洗脱曲线见图 2。结果表明洗脱容易。

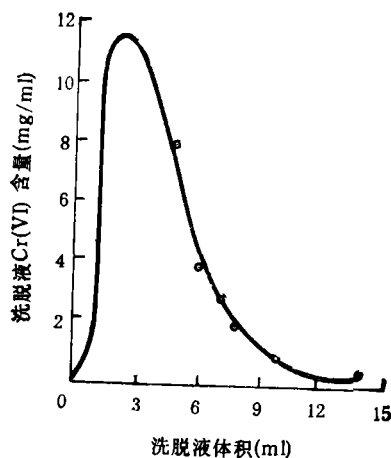


图 2 洗脱曲线

(2) 再生及回收 洗脱后的玉米麸质铁再用  $\text{FeCl}_3$  处理。再生后的玉米麸质铁对  $\text{Cr(VI)}$  的去除率达 99.7% 以上。 $\text{Cr(VI)}$  的洗脱率七次结果都在 92—100% 范围内。洗脱液经加碱,浓缩可回收  $\text{Na}_2\text{CrO}_4$ 。

### 3. 实验室放大试验

放大试验用的是分散在锯末上的玉米麸质铁。由于扩大了表面积,提高了麸质的利用率。试验采用两只内径 8cm 的塑料柱子。装填锯末分散玉米麸质铁 5L (相当于净麸质 2000g)。第一只柱子装填高度 90cm, 第二只柱子装填高度 60cm。含  $\text{Cr(VI)}$  废水取自某厂电镀车间,  $\text{Cr(VI)}$  含量  $50\mu\text{g} \cdot \text{ml}^{-1}$ , 处理结果见表 3。

由结果可见,流过废水总体积 36L, 出口水  $\text{Cr(VI)}$  浓度为  $0.22\mu\text{g} \cdot \text{ml}^{-1}$ , 远低于国家排放标准 ( $0.5\mu\text{g} \cdot \text{ml}^{-1}$ ), 结果满意。

表 3 放大试验结果

试验柱	流过体积 (L)	出口浓度 ( $\mu\text{g} \cdot \text{ml}^{-1}$ )	去除率 ( $\eta$ )
第一柱	4.0	未检出	100
	6.0	0.042	99.9
	9.0	0.18	99.5
两柱串联	9.0	未检出	100
	15.0	0.13	99.6
	20.0	0.18	99.4
	27.0	0.22	99.4

### 三、玉米麸质铁吸附Cr(VI)的机理探讨

玉米麸质含有丰富的蛋白质,其含量在50%左右。该麸质蛋白在通常的水溶液中带有负电荷。它的多种氨基酸残基,如羧基,巯基,酚羟基等能强烈地结合正离子。所以它对重金属阳离子  $\text{Hg(II)}$  有很好的吸附作用<sup>[1]</sup>。当玉米麸质结合上铁以后,它的负电性被中和,使得蛋白质上,在一定条件下带正电的氨基酸残基,如氨基、咪唑基等含氮基团显示作

用。另一方面,大量铁  $\text{Fe(III)}$  吸附和沉积会使蛋白质胶体的 $\zeta$ 电位变号,由带负电的胶体变为带正电的胶体。所以笔者认为,玉米麸质铁对  $\text{Cr(VI)}$  的吸附,既有静电吸附,也有胶体吸附,而且胶体吸附可能占有重要地位。有关玉米麸质铁对  $\text{Cr(VI)}$  的吸附机理是比较复杂的,有待进一步研究。

### 四、结 束 语

用玉米麸质铁处理含  $\text{Cr(VI)}$  废水具有成本低,是活性炭价格的三分之一到五分之一,投资少,处理方法简单,且吸附效果好等特点。为小规模含铬废水的治理提出了一新的方法。

### 参 考 文 献

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## 河流横向混合系数的室内试验

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**摘要** 本文在实验室矩形平直明渠内,对横向混合系数的公式结构进行了探讨。在室内模型内做大量的示踪试验,获得 63 组实验数据,在此基础上确定了关于横向混合系数的准数关系式,并对该式作了分析。由室内模型所归纳的公式和结论,可为天然顺直河流横向混合系数的确定提供参考。

**关键词** 矩形平直明渠;横向混合系数;示踪试验;准数关系式。

研究污染物在河流中横向混合过程的关键,是如何确定横向混合系数,而到目前为止,横向混合系数的研究还很不成熟。人们在估算河流横向混合系数时,至今仍采用下式<sup>[1]</sup>

$$E_x = \alpha_s h u^* \quad (1)$$

式中,  $E_x$  为横向混合系数 ( $\text{m}^2/\text{s}$ );  $h$  为平均

水深 ( $\text{m}$ );  $u^*$  为摩阻流速 ( $\text{m/s}$ );  $\alpha_s$  为无量纲横向混合系数,通常为一常数。

人们认为上面的估算公式在结构上不够完善。有的研究者认为<sup>[2]</sup>,在高紊时,横向混合系数不仅与水深  $h$  和摩阻流速  $u^*$  有关,还可能与河宽  $B$  和平均流速  $\bar{u}$  有关,即

$$E_x / h u^* = \phi(u^* / \bar{u}, B / h).$$

## on Natural Sediments; Effect of Solid Concentration on Adsorption Partition Coefficients.

Zhao Yuanhui (Dept. of Environmental Science, Nanjing University), Lang Peizhen (Dept. of Environmental Science, Northeast Normal University): *Chin. J. Environ. Sci.*, 12(5), 1991, pp. 23—27

Adsorption behavior of organic pollutants in Shonghua River was studied. The solid effect can be attributed to transfer of dissolved solid phase to liquid phase during the course of adsorption partitioning. Based on the results of our experiments, a mathematical model was developed for calculating adsorption partition coefficients (K). Thus, the K values for eleven compounds at different solid concentrations were obtained.

**Key Words:** adsorption, solid concentration, adsorption partition coefficient.

## An Experimental Study on Treatment of Chromic Slag with the Way of Burning for Making Portland Cement.

Xi Yaozhong (Research Institute of Cement, Chinese Academy of Building Materials, Beijing): *Chin. J. Environ. Sci.*, 12(3), 1991, pp. 27—31

Chrome slag discharged from dichromate plants contains 0.1—0.3% water-soluble  $\text{Cr}^{6+}$  and 0.2—0.8% acid-soluble  $\text{Cr}^{6+}$ , which is a nasty pollutant. This paper presents a new method for treatment of chrome slag containing  $\text{Cr}^{6+}$  by means of adding a small amount of it to raw meal for making Portland cement. In the experiments,  $\text{Cr}^{6+}$  removal rate of chrome-slag cement burned in a laboratory furnace or a small shaft kiln were obtained, the dissolved amounts of water-soluble  $\text{Cr}^{6+}$  from hardened cement cubes or from those mortar were analyzed, and the stability of reduced chrome in cement under weathering was observed. The results demonstrate that the removal rate of  $\text{Cr}^{6+}$  by burning is over 90%. If total  $\text{Cr}_2\text{O}_3$  in cement is below 1%, the dissolved  $\text{Cr}^{6+}$  concentration from the cement will not exceed 0.5 mg/L for sewage. If total  $\text{Cr}_2\text{O}_3$  is below 0.4%, the  $\text{Cr}^{6+}$  concentration will not exceed 0.05 mg/L for drinking water. The reduced chrome in hardened cement is stable under a long-term weathering, so the method is feasible for treating chrome slag.

**Key Words:** chrome slag, cement, treatment.

## Removal of Cr(VI) from Wastewater with Fe-modified Corn Gluten.

Liu Manying, Zhang Deqing, Kang Weijun (Hebei Medical College): *Chin. J. Environ. Sci.* 12(5), 1991, pp. 32—34

This paper introduces a new method for the removal of Cr(VI) from wastewater by using Fe-modified corn gluten. The experimental results show that the rate of removal can reach 99.9% at pH 2—10 and flow rate of 5—28 ml/min. and the saturated capacity was determined to be 27 mg/g (measured by Cr(VI)). The results of

enlarged test of true wastewater are satisfactory. The adsorbed Cr(VI) can be eluted by  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (0.3M) and then the material can be reused. In view of the properties of the material, the method has the prospect of becoming a cheap and effective one for the treatment of Cr(VI)-containing wastewater.

**Key Words:** corn gluten, chromium, wastewater treatment.

## Laboratory Study on Transverse Mixing Coefficient of Rivers.

Mu Jinbo, Hou Kefu (Department of Environmental Science & Engineering, East China Institute of Technology): *Chin. J. Environ. Sci.*, 12(5), 1991, pp. 34—37

The formulary structure about transverse mixing coefficient of rivers has been studied at the laboratory model of straight rectangular open channel. In the model, a lot of trace experiments were performed so that 63 groups of data were obtained. On the basis of the experiments, the relation for transverse mixing coefficient was offered and analyzed. The empirical formulation and some conclusions induced by the model will provide reference for ascertainment of the transverse mixing coefficient in natural streams.

**Key Words:** transverse mixing coefficient, empirical formulation, rectangular straight channel, stream.

## A Research on the Natural Resource Catalysts Used in Diesel Engine Emission Purification.

Xu Kaili, Wang Bingquan (Northeast University of Technology): *Chin. J. Environ. Sci.*, 12(5), 1991, pp. 38—41

Several types of natural resource catalysts were prepared by using two kinds of minerals containing both of rare-earth and transition metal element or the transition metal element only. Selection and activity assessment was carried out on a diesel engine platform. Experimental results show that ZC-1 catalyst and ZC-4 catalyst have good characteristics of temperature, space velocity, thermostability and resistance to carbon concentration, and ZC-1 is better. ZC-1 contains oxides of rare-earth metal and transition metal, and ZC-4 contains oxides of transition metal and co-catalyst. Primary investigation on the life time of ZC-1 catalyst showed that, for 700 hours, there was no activity decrease observed.

**Key Words:** engine emission, catalytic purification, nature resource catalyst.

## Study on the Production of Activated Carbon from Straw Pulp and Paper Black Liquor.

Yang Runchang, Zhou Shutian (Dept. of Chemical Engineering, Xiangtan University): *Chin. J.*