土壤中铝的溶出及形态研究*

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摘要　用连续提取法研究1 mol/L KCl，1 mol/L NH_4Ac，1 mol/L HCl和0.5 mol/L NaOH 4种化学浸提液对土壤中铝的溶出。溶出铝用羊毛铬花青R比色法测定。结果表明，铝的溶出量与土壤类型、总铝、有机质含量等因素有关。1 mol/L KCl浸提液对酸性土能溶出一定量的交换态铝，而对非酸性土则不能溶出或铝溶出量极微。0.5 mol/L NaOH浸提出的铝量与总铝量之间有显著相关性。

关键词　土壤，铝的溶出，化学形态。

铝是土壤中存在的主要元素之一。由于母质、成土过程和人为影响各异，因而土壤性质发生分异，影响土壤铝含量及存在的形态。在环境中铝的迁移转化规律，可利用性和对生物的毒性，一般不取决于总量，而与其存在形式或化学形态有关。土壤溶出的无机单聚体铝，如Al^{3+}，$Al(OH)^{2+}$，$Al(OH)_2^+$ 等对生物毒性较大[1]，有人对酸雨地区土壤活性铝的溶出，形态及其分布进行了研究[2-4]。本研究采用连续提取法研究土壤铝的溶出，羊毛铬花青R比色法测定土壤浸提液中的铝，对不同类型土壤铝的溶出及其形态进行初步探讨。

1　材料和方法

1.1　供试土壤

土壤试样按常规方法采自不同地区。土壤类型、有机质、总铝和pH值列于表1。

表1　土壤类型、有机质、总铝和pH值

土　壤	有机质(%)	总铝(%)	pH值
砖红壤	1.10	15.48	5.38
黄色红壤	1.39	11.23	4.88
黄红壤	0.55	11.42	4.52
石灰岩土壤	1.06	12.41	5.30
黄壤	0.53	6.31	8.52
黄棕壤	0.86	6.48	7.82
栗钙土	0.84	5.46	8.48
暗棕壤	3.10	7.50	6.29

1.2　土壤铝的浸提方法

土壤预处理和4种土壤浸提液配制主要按文献[2]进行，但在土壤浸提过程中采用连续提取方法，具体操作步骤如下：

(1) 1 mol/L KCl提取　取0.200 g土壤于离心管中，加入10.0 ml浸提液，在康氏振荡器上振摇30 min后以5000 r/min离心分离15 min，倾出上清液，用去离子水洗涤残渣。

(2) 1 mol/L NH_4Ac提取　取(1)中残渣，用10.0 ml浸提液，振摇后离心分离，倾出清液，洗涤残渣。

(3) 1 mol/L HCl提取　取(2)中残渣，用10.0 ml浸提液，振摇后离心分离，倾出清液，洗涤残渣。

(4) 0.5 mol/L NaOH提取　取(3)中残渣，用10.0 ml浸提液，振摇后离心分离，倾出清液。

1.3　铝的分析方法

(1) 显色液　称取0.050 g羊毛铬花青R (ECR)粉末和0.180 g十六烷基三甲基溴化铵(CTA)表面活性剂，用0.1 mol/L HAc-NaAc缓冲溶液定溶于100 ml容量瓶中，得1.0 mmol/L ECR＋5.0 mmol/L CTA显色液[3]，或

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只取 ECR，同法配制 1.0 mmol/L ECR 显色液(用于测定 Al 含量较高的样品)[2]。

(2) 抗坏血酸(0.1%) 称取 0.050 g 抗坏血酸，置于 50 ml 容量瓶中，用 0.01 mol/L H_2SO_4 稀至刻度。此溶液用时配制。

(3) 缓冲液 称取 68 g NaAc·$3H_2O$，用去离子水溶解，再加 20 ml 1mol/L HAc，最后用去离子水稀至 500 ml。此溶液的 pH 值为 6。

(4) ECR-CTA 比色法 于 25 ml 容量瓶中加入 10 ml 去离子水及铝标准溶液(0，0.5，1.0，1.5，2.0，2.5 μgAl^{3+})，加入 0.5 ml 抗坏血酸(0.1%)，摇匀，放置数分钟后，加入 5.0 ml 缓冲液，摇匀，再加 2.5 ml 显色液，用去离子水稀至刻度，约 15 min 后于 582 nm，1 cm 比色皿，试剂空白参比，测吸光度。工作曲线的线性回归方程为 $y=7.185x-0.124$，相关系数 $r=0.9986$。

(5) 提取液中铝的分析 用 1 mol/L KCl、1 mol/L NH_4Ac 提取液分离后，取 5.00 ml 提取液置于 50 ml 容量瓶内加水至刻度。1 mol/L HCl，0.5 mol/L NaOH 提取液分离后，取 2.00 ml 提取液，加水至约 35 ml，分别用 0.5 mol/L NaOH，1 mol/L HCl 调节 pH 值约 3 左右，转至 50 ml 容量瓶内，用水稀至刻度。取一定体积的上述稀释液，用 ECR-CTA 或 ECR 比色法测定提取液中的铝含量。4 种提取液中铝的回收率为 93%—98%之间。

2 结果和讨论

土壤中铝的溶出及其含量的分析结果列于表 2。

2.1 土壤铝的溶出及其化学形态

表 2 土壤中铝的溶出及其含量

土壤类型	浸出 Al 量(μg/g)				占总 Al 百分数(%)			
	KCl	NH_4Ac	HCl	NaOH	Al^{3+}	$Al(OH)^{2+}$ $Al(OH)_2^+$	$Al(OH)_3^0$	Al-HA
砖红壤	36	403	2844	6093	0.023	0.26	1.84	3.94
黄色红壤	72	569	10219	6657	0.064	0.51	9.10	5.93
黄红壤	132	538	6058	4313	0.120	0.47	5.30	3.78
石灰性土壤	18	523	7438	4157	0.015	0.42	5.99	3.35
黄壤	24	432	2829	625	0.038	0.68	4.48	0.99
黄棕壤	0	250	2200	380	0	0.39	3.40	0.59
栗钙土	0	250	4975	613	0	0.46	9.11	1.12
暗棕壤	0	190	1650	1490	0	0.25	2.20	1.99

在化合物中铝以三价形式存在。土壤中活性铝的溶出，常用 4 种化学浸提液[2—4]。文献[2]归纳出这几种提取液对活性铝的溶出，并用差减法估算重庆、贵阳地区土壤中活性铝溶出的形态分布百分率。根据不同浸提液对铝的溶出，采用连续浸提法，土壤铝的溶出及其形态如下：1 mol/L KCl 提取的主要是三价铝离子(Al^{3+})或称为交换态 Al[2,4]；1 mol/L NH_4Ac 提取的主要是单聚体羟基 Al，如 $Al(OH)^{2+}$，$Al(OH)_2^+$ 及可溶性的富非酸铝等，称为单聚体羟基态 Al[3]；1 mol/L HCl 提取的主要是酸溶无机 Al，如 $Al(OH)_3^0$；0.5 mol/L NaOH 提取的主要是腐殖酸 Al。

2.2 铝的溶出与土壤类型

土壤铝的溶出量与土壤类型有关。4 种浸提液对不同土壤铝的溶出量有很大差异。浸提液对土壤铝的溶出量为 KCl<NH_4Ac<HCl 和 NaOH。1 mol/L KCl 浸提液对各类红壤的交换态 Al 的溶出量较高，而对栗钙土、黄棕壤和暗棕壤未提取出交换态 Al。红壤多含铁铝成分，一般多呈酸性或强酸性，而栗钙土有强烈石灰性反应，土壤呈碱性。1 mol/L KCl 浸提液对酸性土能溶出一定量交换态 Al，而对非酸性土壤则不能溶出或 Al 的溶出量极微[2]，说明土壤类

型对铝的溶出有一定关系。

2.3 铝的溶出与总铝

不同类型土壤溶出铝的各种形态占总 Al 的百分率变化较大(参见表 2)。土壤溶出的 Al^{3+}，$Al(OH)^{2+}$，$Al(OH)_2^+$ 含量占总 Al 的比例很小。各浸提液溶出的 Al 量(μg/g)与土壤总 Al(%)之间的相关系数列于表 3。结果说明土壤溶出 Al 量与总 Al 量有一定关系，其中用 0.5 mol/L NaOH 浸提液溶出 Al 量与土壤总 Al 有较显著相关性。

表 3　土壤溶出 Al 量与总 Al 量关系

浸提液	相关系数 (R)	显著性水平 (α)
1 mol/L NH_4Ac	0.6220	0.1—0.05
0.5 mol/L NaOH	0.9074	<0.01
1 mol/L KCl+1 mol/L NH_4Ac	0.6190	0.1—0.05
4 种浸提液	0.6835	0.1—0.05

2.4 铝的溶出与有机质含量

土壤中有机质含量不同，铝的溶出量也不同。在多数情况下，有机质含量较多，4 种土壤浸提液溶出的铝量普遍较高。土壤有机质同溶出铝形成的络合物与酸度条件有关。当 pH 值为 4.5—5.0 时，有机质中的腐殖酸能络合大量铝，但是，当酸度进一步增加时，络合铝的可溶性与流动性会降低[2]。因此，土壤中有机质含量与铝的溶出量有一定关系。但同时还受酸度等因素影响。

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3.3 有机物含量变化对工艺性能的影响

水库水的低浊度性质决定了水中有机物质主要以胶体及溶解状态存在，而水中悬浮的有机颗粒相对较少，这对于生物陶粒工艺是有利的。进水浊度低可以延长生物陶粒的运行周期，避免生物膜处于厌氧状态，保证生物活性；而且，水中大量的溶解性有机物可以很容易地被水相传输，使生物膜很快地吸收和降解，因此生物陶粒工艺才能在低温及常温下保持较好的有机物去除率。

从图 1、2 中可以看出，当进水中的 COD、OC 浓度增加时，生物陶粒工艺的出水 COD、OC 含量也随着增加，去除率出现一个短暂的陡升，这说明该对水中有机负荷的增加有一定的承受能力，但这种能力是有限的，出水中的有机物浓度的增加预示着工艺性能的减弱。

4 结论

(1) 以陶粒为载体的生物预处理工艺，在 RHT 为 20 min，水气比为 1∶1，水力负荷为 4—5 $m^3/(m^2 \cdot h)$ 条件下，常温可去除 COD 26.2%，OC 20%，氨氮 80%，SS 60%—70%，温度<3℃时可去除 COD 20%，OC 11.4%，氨氮 50%，SS40%左右，低温时去除率受到一定影响。

(2) 水库水的低浊度和有机物含量较多的性质对于生物预处理是十分有利的。不仅生物预处理工艺处理水中有机物的去除效率得以提高，而且还可以节省混凝剂，简化给水处理工艺，达到低能耗高效率的目的。

(3) 对于册田水库这类低温低浊微污染水源，生物预处理技术是可行的，因此针对原有的传统工艺，结合生物预处理工艺来控制水中有机污染物是今后饮用水处理的一个很有前途的发展方向。

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protection. In addition, the environmental drag were used to explain the model's meaning as well as to discuss the measurement of the environmental drag.

Key words: social rate of return, private rate of return, elasticity of elasticity, environmental discount rate, environmental investment, environmenal improvement, environmental drag.

The Growth and Purification Function of *Eichhornia crassipes* Solms in Oil-refinery Wastewater. Tang Shuyu et al. (Institute of Botany, Jiangsu Province and Chinese Academy of Sciences, Nanjing 210014): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 44—46

The growth of *Eichhornia crassipes* Solms in oil-refinery wastewater has been described in this paper. An influence of COD, a comprehensive index of the pollultant concentration in the wastewater, on the growth of *Eichhornia crassipes* Solms was quantitatively studied. It was found that an optimum working condition for treating oil-refinery wastewater by *Eichhornia crassipes* Solms eco-engineering is established as follows: 65 mg/L<[COD]<131 mg/L; and 262. 6 mg/L of COD at effective critical point.

Key words: *Eichhornia crassipes*, oil-refinery wastewater, purification.

Study on Method of Sister Chromatid Exchange in *Vicia faba* to Detect Environment Mutagen. Kong Zhiming et al. (Dept. of Environ. Sci. and Eng., Nanjing University, Nanjing 210093): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 47—49

The experimental conditions of the Brdu-Feulgen method of SCE in *Vicia faba* root which include the content of Brdu, labelling time of Brdu, the impacts on SCE of the content of hydrochloric acid and time and temperatrue for hydrolysis were studied and discussed in this paper. The best experiment conditions and procedure, which overcome the short-comings of FPG method that is complicated in procedure and, hence, difficult to be popularized, were obtained. In addition, such method was compared with other genotoxicology method in order to probe into the possibility of utilizing such technology to detect environment mutagen.

Key words: *Vicia faba*, SCE, Brdu-Feulgen method.

A Pulse-feed Upflow Anaerobic Sludge Blanket Reactor. Su Yumin et al. (Dep. of Environ. Eng., Taiyuan Univeristy of Technology, Taiyuan 030024): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 50—53

The key parts of Upflow Anaerobic Sludge Blanket Ractor are gas-solids separator and feed system. The goals of this research, in which a conventional continuous feed system was replaced by an intermittent pulse-feed one, are to provide gently hydraulic mixing, to promote hydraulic selection, and to improve the contact between substrate and microorganisms. Pulse-feed method can raise the orgainc load rate as high as 27. 5 gCOD/(L. d), reduce HRT to nearly 3 hrs, and quickly develop granulated sludge in 47 days. It can not cause shock load and intermediates accumulation, as every pulse only releases a small amount of wastewater (1/56 reactor volume), which can not raise the substrate concentration in whole reactor. The pulse-feed also can not cause sever wash-out of sludge, because pulse-feed mi-xing can effectively separate sludge flocs and entrapped gas bubbles, and hence improve sludge settleability. The advantages of enrichment of *methanosarcina* species in the process of granulation are also discussed. At high load rate, *methanosarcina* species do appear in clumps on the granules.

Key words: anaerobic digestion, UASB, pulse-feed, mixing, granulation, *methanosarcina* species.

Study on Biological Pretreatment Method-bio-ceramic Reactor Treating Micro-pollution Source Water at Low Temperature and Low Turbidity. Hu Jiangyong et al. (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 54—56

One of biological pretreatment methods-bio-ceramic reactor (BCR) was used to treat a typical source water with micro-pollution at low temperature and low turbidity. By means of in-situ experiments with the bio-ceramic reactor, it was found that: the organic matter (OC or COD), ammonia, SS in the source water could be removed about 20%—30%, 60%—70% and 80%, respectively. Removl efficiency could be reduced at low temperature. Low turbidity and high concentration of organics in the source water would be benifical to BCR. In general, BCR would be a powerful way to purificate this kind of source water.

Key words: micro-pollution, source water, low temperature, low turbidity, organics, bio-ceramic pretreatment process.

Studies on the Leaching and Species of Aluminum in Soil. Huang Yanchu and Qu Changling (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 57—59

The leaching and chemical forms of aluminum in soil by sequential fraction procedure were studied. Solutions used sequentially to extract Al are inorder of 1 mol/L KCl, 1 mol/L NH_4Ac, 1 mol/L HCl and 0. 5 mol/L NaOH. The spectrophotometric determination of leaching Al was performed with Eriochrom Cyamine RC. It has been found that the type of soil and the amounts of organic materials and total Al in soil have a siginificant effect on the amount of leaching Al. A certain amount of exchangeable Al can be leached from acid soil with 1 mol/L KCl extractant, however, it can not be leached from alkaline soil. The leaching Al extracted with 0. 5 mol/L NaOH is correlated at a high level of siginficance with the total Al in soil.

Key words: soil, leaching aluminum, chemical form.

Efficiency of Fluidized Biofilm Method for Treating Phenolic Wastewater. Yin Jun et al. (Jilin Architechtural and Civil Eng. Institute, Changchun 130021): *Chin. J. Environ. Sci.*, **17**(1), 1996, pp. 60—62

A dynamic experiment was conducted to examine the efficiency of the fluidized biofilm method with home-made carrier for treating phenolic wastewater. The experimental results have shown that COD and phenol were removed on an average over 80% and 90%—100%, respectively, while COD volumetric loading is 4. 0 $kg/(m^3 \cdot d)$, and the final concentrations of COD and phenol in the effluent can meet Chinese Standard of Wastewater dischange permission. The biofilm can adhere quickly to the home-made carrier and the thickness of biofilm is suitable