不同类型土壤对 SO_4^{2-} 吸附特性的研究*

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摘要　为了进一步探讨我国酸沉降对水陆生态环境的影响以及典型地区生态系统对酸沉降的缓冲能力和临界负荷值，笔者对赣、鄂、湘 3 省具有代表性的土壤的 SO_4^{2-} 吸附特性进行了研究。结果表明，红壤，特别是江西省的红壤，吸附 SO_4^{2-} 的能力最强，最大吸附量达 11.52 mg/g 土；其余依次为黄壤、棕红壤、黄褐壤和黄红壤，最大吸附量分别为 11.14，8.83，6.86 和 6.53 mg/g 土；红色石灰壤对 SO_4^{2-} 的吸附能力最弱，最大吸附量仅 3.55 mg/g 土，只及红壤的 30.8%。可以预计，就地区而言，以红壤为主的江西省是我国对酸沉降最敏感的地区之一。

关键词　土壤，pH，SO_4^{2-}，吸附特性，生态环境。

我国是世界燃煤大国，每年直接燃煤约 5 亿 t，煤含硫量一般为 2%左右，有些高硫煤含硫量多达 3%以上。我国的酸雨已相当严重，并呈硫酸型，主要和燃煤造成的大气污染有关。在长江以南，SO_4^{2-} 已成为酸性降雨中的主要组分[1]，其所占比例有时可达降水阴离子组分的 90%，是直接左右降水酸度的一个重要因素。土壤是大气酸沉降的主要受体，H^+ 和 SO_4^{2-} 进入土壤后，对土壤的 pH、离子吸附和表面电荷等理化性质均产生明显影响，继而影响生态环境。本文试图通过对湖南、湖北和江西 3 省多种不同类型土壤的 SO_4^{2-} 吸附特性的研究来评价土壤对酸沉降的缓冲性能和承受能力，为研究我国酸沉降及其对水陆生态环境的影响提供科学依据。

1　实验部分

1.1　材料与试剂

（1）供试土壤　1991—1992 年，从湖南、湖北、江西 3 省采集了具代表性的不同类型土样(0—20 cm)共计 39 份作为测试材料，样品自然风干并经 60 目过筛。表 1 列举了供试土壤的类型及主要理化性质。

（2）100 mol/L SO_4^{2-} 标准液　用分析天平准确称取在 110℃烘烤 2 h 的分析纯无水 Na_2SO_4 14.204 g，无离子水溶解后定容至 1000 ml。试验中所用的系列浓度均由此标准液稀释而得。

表 1　土壤类型及主要理化性质[1)]

省份	土壤类型	样品数	有机质 (%)	CEC (mg/g)	pH (H_2O)	盐基饱和度 (%)
湖北	棕红壤	1	1.05	5.00	4.62	16.18
	红壤	1	1.00	2.57	5.25	9.01
	红壤性土	1	1.13	6.50	5.39	19.01
	黄棕壤性土	2	1.21	5.35	6.80	35.18
	黄棕壤	3	1.28	6.14	6.85	69.65
	暗黄棕壤	2	1.09	5.24	6.94	11.34
	黄褐壤	1	3.01	9.39	7.60	86.20
	棕色石灰壤	2	1.89	7.56	7.70	22.93
	黄壤	1	1.75	7.47	8.04	24.56
	中性紫色壤	1	2.75	8.14	8.30	44.82
湖南	红壤	8	2.60	6.17	5.42	18.49
	黄红壤	1	3.18	6.19	6.50	34.28
	黄壤	2	3.61	7.43	6.60	33.56
	红色石灰壤	1	2.86	6.84	8.20	60.10
	酸性紫色壤	1	1.67	5.06	8.32	10.01
江西	红壤	8	2.75	4.47	5.02	12.93
	黄壤	1	5.77	7.45	5.13	13.51
	棕红壤	2	2.26	4.56	5.25	40.90

1)　表内湖南和江西省的有机质，CEC(阳离子交换量)和盐基饱和度的数据引自参考文献[2，3]；湖北省的引自内部资料**；样品数大于 1 时取平均值

1.2　实验方法

(1)吸附处理　每种供试土壤各秤取 6 份，

* 国家"八五"科技攻关项目

** 湖北省土壤普查办公室编。湖北土壤。1990，内部资料

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每份 10 g，分别加入 100 ml 不同浓度系列的 Na_2SO_4 标准溶液，最终浓度(SO_4^{2-}/g 土)分别为 2.4—4.8 mg，置摇床振荡 2 h(140 r/min)后，于室温下静放 2 h，使其充分平衡，离心 15 min(3500 r/min)，取上清液(即吸附平衡液)过滤后测定其 SO_4^{2-} 的含量。

(2) SO_4^{2-} 的测定　用 $BaSO_4$ 比浊法测定吸附平衡液中 SO_4^{2-} 的浓度，当水样不澄清、不透明时，用浓 HNO_3 消化 3 次(10—15 ml/次)，以去除有机胶质[4,5]。

(3) SO_4^{2-} 吸附量的计算　以标准溶液中 SO_4^{2-} 加入量和土壤本底 SO_4^{2-} 含量之和，减去吸附平衡液中 SO_4^{2-} 的残留量，求得土壤对 SO_4^{2-} 的吸附量。

(4) 吸附等温线的制作　以土壤对 SO_4^{2-} 的吸附量为纵座标，吸附平衡时溶液中 SO_4^{2-} 的浓度为横座标作图，制得吸附等温线，从吸附等温线求得 SO_4^{2-} 的最大吸附量和吸附半饱和时平衡溶液中 SO_4^{2-} 的浓度。

2 结果与讨论

2.1 3 省土壤的分布状况及其对 SO_4^{2-} 的吸附特性

江西是我国红壤分布最广的省份之一，其红壤土类的面积占全省土壤总面积的 70.69%，是该省农业生产和今后总体开发利用的重要土壤资源[2]。在该省所采集的 11 个土样中，红壤占了 73%(8 个)。

湖南省典型的地带性土壤亦是红壤，但由于自然条件复杂，生物气候条件南北有异，东西不同，从而导致红壤的脱硅富铝化过程发生相应的变化，红壤逐渐黄化，渐变为黄红壤，黄壤[3]等。该省共采土样 13 个，其中红壤 8 个，黄壤 2 个，黄红壤，紫色壤和石灰壤各 1 个。

湖北省的土壤类型最多，变化幅度较大，没有明显的地带性土壤，在所调查的 15 个土样中，土壤类型多达 10 种。

表 2 提供了各地不同土壤的 A1 含量和 pH 值以及土壤对 SO_4^{2-} 的吸附测试结果。数据表明，土壤的类型不同，对 SO_4^{2-} 的最大吸附量不一样，同一类型的土壤因省份的不同最大吸附量也有差异(如 B-1 和 X-3，N-1 和 X-1，以及 N-3 和 X-2 等)。就红壤而言，不同母质发育的红壤，其红色风化层，颜色，酸碱性以及表面吸附盐基的程度等均有差异。相比之下，江西土壤的酸度最大，对 SO_4^{2-} 的吸附能力也最强。不同类型土壤对 SO_4^{2-} 吸附量大小的排列顺序各省基本一致，即：红壤类＞黄壤类＞其他类。红色石灰壤对 SO_4^{2-} 的吸附能力最弱，最大吸附量仅 3.55 mg/g。

2.2 土壤的酸碱度对 SO_4^{2-} 吸附的影响

土壤的酸碱度是土壤的基本化学性质之一，对土壤地球化学过程中元素的淋溶迁移和富集，氮磷等主要养分的转化和释放以及土壤对 SO_4^{2-} 的吸附能力等均有明显影响。比较表 2 中 pH 值与 SO_4^{2-} 吸附量的数据发现，两者之间呈明显负相关，即土壤的 pH 值越大，对 SO_4^{2-} 的吸附作用越小。在所测试的 pH 范围内，土壤对 SO_4^{2-} 的吸附作用(Y)随 pH 值(X)的下降而增加，两者间的回归方程依省份的不同而略有差异(表 3)。其中湖北省土壤的相关性略差，主要因该省土壤的酸碱性变化幅度较大，土壤类型较多所致。

2.3 土壤阳离子交换量与 SO_4^{2-} 吸附的关系

土壤阳离子交换量的大小反映了土壤对阳离子形态养分容量的大小和土壤保肥能力的强弱。通常情况下，土壤溶液中游离的 H^+ 和 OH^- 离子与土壤胶体吸附的交换性阳离子(如交换性 H，Al，Ca，Mg，K，Na 等离子)保持着动态平衡。土壤溶液中 H^+ 的多少受土壤交换性 H^+ 和 Al^{3+} 的制约，而后者在调节或矫正土壤的酸度中起着不可忽视的作用。由表 1 的数据可见，本研究中所调查的土壤的阳离子交换量多数波动在 4.8—9.6 mg/g 之间，属中等范围，仅江西的红壤和棕红壤以及湖北红壤的阳离子交换量不足 4.8 mg/g，可能与采样地区的母质和土壤中含沙粒较多，降水量较大，风化淋溶作用较强，土地的利用指数较高有关。

表 2　土壤的铝含量及其对 SO_4^{2-} 的吸附

样品号	土壤类型	Al_2O_3		SO_4^{2-} 含量		pH (H_2O)
		Al_T ($\times10^{-3}$ mg/g)	Al_d (mg/L)	A[1]	C[2]	
B-1	棕红壤	1.63	0.138	8.83	1032	4.62
B-2	红壤	1.24	0.074	7.10	864	5.25
B-3	红壤性土	0.60	0.031	5.18	720	5.39
B-4	黄棕壤性土	3.33	0.271	4.66	926	6.80
B-5	黄棕壤	1.29	0.105	5.18	605	6.85
B-6	暗黄棕壤	0.39	0.016	4.51	917	6.94
B-7	黄褐壤	0.59	0.040	6.86	792	7.60
B-8	棕色石灰壤	0.98	0.062	5.09	720	7.70
B-9	黄壤	0.28	0.002	7.54	1032	8.04
B-10	中性紫色壤	0.41	0.015	4.03	672	8.30
N-1	红壤	4.04	0.085	7.73	1090	5.42
N-2	黄红壤	1.84	0.143	6.53	768	6.50
N-3	黄壤	0.44	0.016	5.28	1176	6.60
N-4	红色石灰土	0.60	0.041	3.85	965	8.20
N-5	酸性紫色壤	0.32	0.007	5.81	768	8.32
X-1	红壤	5.81	0.141	11.52	1598	5.02
X-2	黄壤	5.89	0.417	11.14	1272	5.13
X-3	棕红壤	1.68	0.118	6.48	922	5.25

1)　土壤 SO_4^{2-} 最大吸附量(mg/g 土)　2)　半饱和时吸附平衡液中 SO_4^{2-} 的浓度(mg/L)

表 3　土壤 pH(X)与其 SO_4^{2-} 吸附量(Y)之间的回归分析

土壤来源	样品数	r	R^2(%)	$Y=a+bX$
湖北省土壤	15	−0.4586	21.03	$-0.1767X+8.9213$
湖南省土壤	13	−0.7715	59.52	$-0.2954X+10.5643$
江西省土壤	11	−0.6242	38.96	$-0.0365X+6.2045$

分析表 2 中，Al_2O_3 和 SO_4^{2-} 含量的相关性可以看出，土壤对 SO_4^{2-} 的吸附量和土壤中 Al 含量的关系也较密切，结果见表 4。

表 4　土壤 SO_4^{2-} 吸附(X)与 Al 含量(Y)之间的回归分析

土壤来源	样品数	r	R^2(%)	$Y=a+bX$
湖北省土壤	15	0.4400	19.36	$10.7200+6.4683X$
湖南省土壤	13	0.7948	63.18	$9.6666+16.3494X$
江西省土壤	11	0.6532	42.67	$9.2978+24.9031X$

3　小结

由于土壤的性状各异，不同类型的土壤对 SO_4^{2-} 的吸附能力差异显著，和土壤的 pH 值以及 Al 的含量明显相关。红壤类土壤吸附 SO_4^{2-} 的能力最强。不同地区的红壤又有地区性差别，江西省的红壤吸附 SO_4^{2-} 的量高于湖南红壤和湖北红壤，这是气候因素与地球化学过程长期作用的结果。可以预计，就地区而言，以红壤为主的江西省是我国对酸沉降最敏感的地区，其水陆生态系统遭受酸沉降污染的危害将居全国之首。

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Abstracts

Chinese Journal of Environmental Science

Joint Production Technology for Resource-Transfer of Paper-Making Black Liquor. Sun Lianchao and Mu Huanzhen et al. (EIA Unit, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 1—2

The black liquor resource-transfer technology is an original conception. Through recovering resources to treat pollution, it transforms the utilization of straw from single cellulose paper making into comprehensive use of cellulose, lignin, glycans and other resources. At the same time, black liquor pollution is thoroughly treated without second pollution, the components of black liquor are separated and many kinds of raw materials produced. It provides a vast prospect for further development and has remarkable environmental, social and economic benefits.

Key words: joint production technology, paper making black liquor, recovering resources.

Inhibition of Sulphates and Chlorides to Anaerobic Digestion. Wang Jusi et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 3—7

The effects of sulphates (SO_4^{2-}) and Chlorides (Cl^-) concentration on the anaerobic digestion process in a batch digestion reactor were studied. The experimental results indicate that the digestion system would be normally running when the concentration of daily addition was less than 144 mg/L for SO_4^{2-} and 3195 mg/L for Cl^- and the permissible accumulated amount in the digestion system was 300 mg/L for SO_4^{2-} and 20000 mg/L for Cl^-, respectively. No inhibition effect on the anaerobic system occurred when the loading of SO_4^{2-} and Cl^- to activated sludge (dry weight) was less than 5.55 g/kg (SO_4^{2-}/VS) and 58.6 g/kg (Cl^-/VS), respectively.

Key words: sulphates, chlorides, anaerobic digestion, inhibition effects.

Relationship between Organic Acid Content in Paddy Soil and Release of Methane from It in the Red Earth Hilly Areas in South China. Wang Weidong et al. (Changsha Institute of Agricultural Modernization, Chinese Academy of Sciences, changsha 410125): *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 8—12

Organic acid content (OAC) in paddy soil and release of methane (ROM) from it in the red earth hilly areas in South China were determined with spectrophotometry and microcomputer controlled gas chromatography, respectively. Four fertilization plots were found to have a consistent temporal trend of variation in OAC but not in ROM, and to have a correlativity between OAC and ROM as follows: the plot applied fully with organic manure ($r=0.981$)>the plot fertilized in a normal way ($r=0.855$)>the plot applied fully with chemical fertilizers ($r=0.353$)> the plot applied with a biogas residue ($r=0.0213$). Four water management plots were found to have a consistent temporal trend of variation in both OAC and ROM, except for the plot of constant moisture, and to have a correlativity between OAC and ROM as follows: 10 cm deep water covered plot ($r=0.993$)> frequently drained plot ($r=0.910$)>3 cm deep normal water covered plot ($r=0.714$)> constant moisture plot ($r=0.00526$). OAC has the same vertical distribution in soil depth as that of ROM.

Key words: organic acid content, release of methane, paddy field, greenhouse gas.

Characterization of the Adsorption of Sulfates onto Different Types of Soil. Kuang Qijun et al. (Institute of Hydrobilogy, Chinese Academy of Sciences, Wuhan 430072): *Chin. J. Environ. Sci.*, 1995, **16**(4), pp. 13—15

The characteristics of sulfates adsorption onto the representative types of soil in the three provinces of Jiangxi, Hubei and Hunan were studied in order to further understand the effects of acid deposition on aquatic ecosystems in China, and the capacity of ecosystems in typical areas to buffer an acid deposition and their values of critical loading. The results show that the red soil, particularly from Jiangxi Province, has the strongest capacity of adsorbing sulfates with a maximum adsorption capacity of 11.52 mg/g, and others in an order of decreasing maximum adsorption capacity are yellow soil of 11.14 mg/g, brown-red soil of 8.83 mg/g, yellow-brown soil of 6.86 mg/g, yellow-red soil of 6.53 mg/g, and red-lime soil of 3.55 mg/g which is only 30% of that for red soil and the weakest one. It is expected that Jiangxi Province where red soil is dominately distributed would be one of the areas which are most sensi-

tive to acid deposition in this country.

Key words: sulfate ions, soils, adsorption capacity, aquatic ecosystems.

Method for Testing the Photodegradability of Herbicides Adsorbed on HPTLC Plates. Yue Yongde (Dept. of Environ. Protection, Anhui Agriculture University, Hefei 230036): *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 16—18

A rapid and effective method to detect the photodegradability of herbicides in an adsorption state was developed with a high performance thin layer chromatography (HPTLC) technique. Two herbicides, chlortoluron and fluorodifen, were applied directly on a silica gel 60 F254 high performance thin layer plate (10X20cm) by Linomat Ⅳ in a dosage of 400—800 ng per slit, then irradiated under natural sunlight, and then the HPTLC plates were developed and measured with a DESAGA 60 Scanner. The photolytical dynamics of chlortoluron and fluorodifen, the optimal dosage and other test conditions were also described in this paper.

Key words: herbicides, high performance thin layer chromatography (HPTLC), chlortoluron, fluorodifen.

Treatment of Zn^{2+} Contaminated Wastewater with a Method of Sulfate Bio-reduction. Ma Xaohang et al. (Zhejiang Institute of Microbiology, Hangzhou 310012): *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 19—21

A process for the treatment of Zn^{2+} containing wastewater by sulfate-reducing bacteria in an upflow anaerobic sludge bed reactor has been studied. When the concentrations of COD and Zn^{2+} in influent were 320 mg/L and 100 mg/L, respectively, the reactor could be successfully operated. Under this condition the removal rates of COD and Zn^{2+} were 73.8% and 99.8% respectively. When the concentration of Zn^{2+} was less than 500 mg/L the reactor was operated successfully. Whereas when the Zn^{2+} concentration in influent was higher than 500 mg/L the activity of the sulfate-reducing bacteria was suppressed by Zn^{2+}. When the Zn^{2+} concentration was 500 mg/L and the retention time was 9 h, the reactor had a volume removal rate of Zn^{2+} reaching as high as 1329 mg/(L • d).

Key words: sulfate reducing bacteria; heavy metal wastewater; upflow anaerobic sludge bed reactor.

Study on the Characteristics of a New Class of Double Hydroxyl Stratified Clay Materials for Removing SO_2 from Flue Gas. Chen Yinfei et al. (Zhejiang University of Technology, Hangzhou 310014): *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 22—25

An experimental study was conducted on the desulfurization characteristics of a synthesized class of double hydroxyl stratified clays as a desulfurizer of high temperature flue gases. The results show that after roasted at a high temperature the materials had a higher capacity of desulfurization, a higher rate of SO_2 adsorption, and a higher selectivity to SO_2. By studying the reaction rates at different temperatures, the optimum temperature for each of the stratified double hydroxides (SDH) was found to be 700℃ for NiAl SDH and 750℃ for both ZnAl SDH and ZnMgAl SDH. The selectivity to SO_2 was found to increase with the temperature rising from 500℃ to 750℃. During the first 10 minutes after a regeneration, the SDHs had essentially an unchanged reaction rate and an insignificantly decreased capacity of desulfurization.

Key words: clay, stratified double hydroxides, desulfurization, SO_2, flue gas.

BOD/DO Mathematic Models for the Water Quality of Lake Moshuihu in Wuhan City and Their Parameters Identification. Mao Rongsheng et al. (Dept. of Rivers, Wuhan University of Hydraulic and Electric Engineering, Wuhan 430072): *Chin. J. Environ, Sci.*, **16**(4), 1995, pp. 26—31

In terms of hydrology, water quality and topography, the Moshuihu Lake in Wuhan City was zoned into five sub-lake areas, for each of which a BOD/DO mathematic model of a scatter structure was set up, together with a method developed for identifying the parameters of the models. The simulation study and model testing gave satisfactory results. Systematology and microcomputerized programming operation were applies as an analysis was made. The developed models were found to meet the needs for planning and managing the water quality of the lake.

Key words: lake, water quality, BOD/DO model, parameters identification, simulation.

Formation of Chloroform during Water Disinfection with Chlorine Dioxide. Wang Yongyi et al. (Dept. of Environ. Eng., Qingdao College of Architecture and Construction Engineering, Qingdao 266033): *Chin. J. Environ. Sci.*, **16**(4), 1995, pp. 32—34

The results show that chlorine reacts with organic