

土壤中硒的形态^{*}

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摘要 3种江苏省土壤,即潮盐土、灰潮土和黄棕壤原土硒和外加硒的形态分布研究结果表明,原土硒主要分布在残渣态 F_5 上,3种土壤的 F_5 的百分含量均达全量硒的80%左右,而外加硒经4个月培养后相对均匀地分布于可溶态 F_1 (黄棕壤例外),交换态 F_2 、氨水提取态 F_3 和残渣态 F_5 上。2种处理下硒形态分布与土壤pH值、粘粒和游离氧化铁含量有一定关系。pH值是潮盐土 \approx 灰潮土 $>$ 黄棕壤,粘粒及游离氧化铁含量是黄棕壤 $>$ 潮盐土 $>$ 灰潮土, F_1 、 F_2 的百分含量是潮盐土、灰潮土 $>$ 黄棕壤,而 F_3 、 F_5 的百分含量是黄棕壤 $>$ 潮盐土 $>$ 灰潮土。

关键词 硒,土壤,形态。

硒的丰缺与动物和人类的健康有着密切的关系。不同性质的土壤原土硒和外加硒有不同的形态分布特征。土壤硒形态分布不同会导致植物对土壤硒的吸收利用程度上的差异。研究不同土壤中硒形态分布以及土壤性质对硒形态分布的影响,对人们准确判断植物缺硒的土壤类型和分布,改良硒土壤,防止缺硒病等措施可提供一定的理论依据。然而,土壤硒的研究一般较其它元素晚,对不同土壤中硒形态分布的研究开展较少。本文选用江苏省境内3种土壤:潮盐土、灰潮土和黄棕壤,作了土壤原土硒和外加硒形态变化对比的研究,并分析了土壤性质对硒形态分布的影响。

1 材料与方法

1.1 供试土壤

潮盐土(0—20cm,下同)采用启东市寅阳乡,灰潮土采自泰县大冯乡,黄棕壤采自江宁县庄里乡。3种土壤的基本理化性质列于表1。

1.2 试验方法

试验分2个处理。一个用原土经风干、磨细过20目筛孔后直接进行硒的各种形态的连续提取。一个是加入 Na_2SeO_3 水溶液使土壤含外加硒为 1mg/kg 土,并保持田间持水量的70%,于自然温度下培养4个月。采集的土样经风干、磨细并过20目筛孔,再进行硒的各种形态连续提取。

硒的各种形态的连续提取法主要参照了 Hamdy 和 Gissel-Nielsen 的步骤进行^[1],但在提取

时间和无机酸的种类上有所不同。

表1 土壤基本理化性质

土壤	pH	有机质 (%)	CaCO_3 (%)	粘粒 (%)	游离氧化铁 (%)	全硒 (mg/kg 土)
潮盐土	7.80	1.55	2.32	15.57	1.32	0.163
灰潮土	7.75	1.27	0.50	9.10	0.62	0.153
黄棕壤	6.21	1.02	0.00	41.16	2.57	0.155

(1)可溶态 $\text{Se}(F_1)$ 用 0.2mol/L 的 K_2SO_4 溶液振荡浸提16h后离心分离,倾出清液。

(2)交换态 $\text{Se}(F_2)$ 取上步残渣,用 0.05mol/L 的 KH_2PO_4 溶液振荡浸提16h后离心分离,倾出清液。

(3)氨水提取态 $\text{Se}(F_3)$ 取上步残渣,用 0.05mol/L 的 $\text{NH}_3 \cdot \text{H}_2\text{O}$ 溶液振荡16h后离心分离,倾出清液。

(4)盐酸提取态 $\text{Se}(F_4)$ 取上步残渣,用 6mol/L 的 HCl 溶液振荡浸提16h后离心分离,倾出清液。

(5)残渣态 $\text{Se}(F_5)$ 取上步残渣,用 H_2SO_4 — HClO_4 消煮提取。

对原土硒 F_1 、 F_2 、 F_3 、 F_4 形态的硒含量采用 DDB 气相色谱法测定,对原土硒的残渣态 F_5 和外加硒的各种形态硒含量采用 DDB 紫外分光光度法测定^{**}。

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^{**} 周溶。用紫外分光光度法和气相色谱法测定土壤含硒量。南京农业大学硕士论文。1990

2 结果与讨论

图 1—5 是土壤原土硒和外加硒 2 种处理下 F_1 — F_5 形态硒占全量硒的百分率。

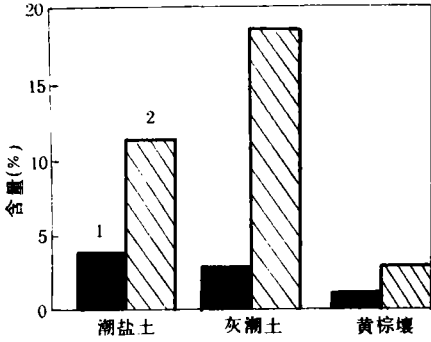


图 1 K_2SO_4 -Se(F_1) 百分含量
1. 原土硒处理 2. 外加硒处理

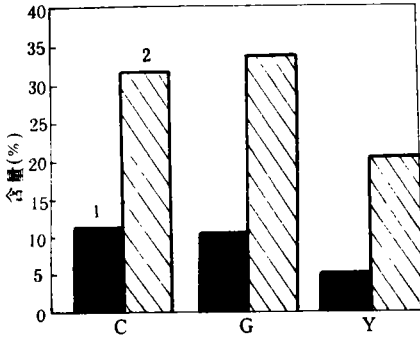


图 2 KH_2PO_4 -Se(F_2) 百分含量
1. 原土硒处理 2. 外加硒处理
C. 潮盐土 G. 灰潮土 Y. 黄棕壤

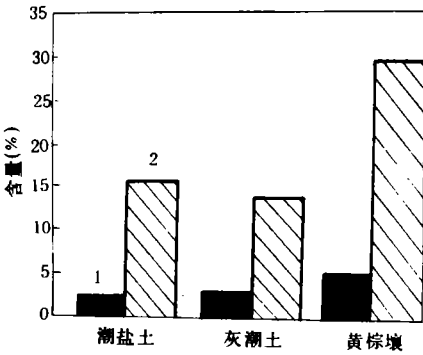


图 3 $NH_3 \cdot H_2O$ -Se(F_3) 百分含量
1. 原土硒处理 2. 外加硒处理

由图 1、2 可见,在 2 种处理下,3 种土壤硒形态分布特征基本一致,可溶态 K_2SO_4 -Se 和交

换态 KH_2PO_4 -Se 的百分含量均是潮盐土和灰潮

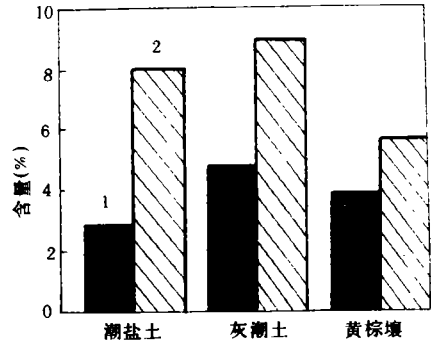


图 4 HCl-Se(F_4) 百分含量
1. 原土硒处理 2. 外加硒处理

土 > 黄棕壤。经培养后的外加硒 F_1 、 F_2 百分含量都高于原土硒,其中以灰潮土增加量最高,潮盐土次之,黄棕壤最小。这一次序与 3 种土壤中的粘粒含量和游离氧化铁的含

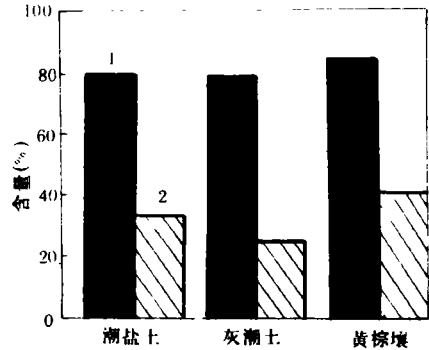


图 5 residue-Se(F_5) 百分含量
1. 原土硒处理 2. 外加硒处理

图 3 为 2 种处理下 3 种土壤氨水提取态 $NH_3 \cdot H_2O$ -Se 的百分含量。由图 3 可见,无论是原土硒还是外加硒, F_3 的百分含量均是黄棕壤 > 潮盐土、灰潮土,外加硒的 F_3 又明显高于原土硒,其中以黄棕壤的最为突出。一般认为 $NH_3 \cdot H_2O$ 浸提液 F_3 为吸附于某些有机化合物上的硒。由表 1 可知,3 种土壤有机质含量以黄棕壤最低,而 F_3 的含量却以黄棕壤最高。对于这一点,笔者认为可能是由于潮盐土、灰潮土都含有一定量的 $CaCO_3$,而钙与腐殖质胡敏酸易形成溶

解度较小的化合物^[2],致使腐殖质与硒结合量减少。而在黄棕壤中不含 CaCO_3 成分,就不会出现上述现象,所以,结果反而使黄棕壤的 F_3 含量较高。实验表明,用 0.05mol/L 的 $\text{NH}_3 \cdot \text{H}_2\text{O}$ 浸提潮盐土、灰潮土所得的离心清液较清且透明,而黄棕壤的离心清液呈褐色,加酸后出现絮状褐色沉淀。笔者在对黄棕壤外加硒形态分布影响因素试验中也发现,经添加 CaCO_3 后,黄棕壤外加硒 F_3 的百分含量较对照(未施添加剂)下降了约 10% 之多。这些亦可证明潮盐土、灰潮土由于 CaCO_3 的影响,使硒与腐殖质结合量相对较少,而黄棕壤中与腐殖质结合硒量相对较多。

图 4 为 3 种土壤在 2 种处理下的盐酸浸提液中硒的百分含量。由图 4 可见,与前 3 种形态分布一样,该形态也出现外加硒的百分含量高于原土硒,但提高幅度很小。

图 5 列出了 3 种土壤原土硒和外加硒的残渣态百分含量。由图 5 可见,2 种处理下 F_5 的百分含量均以黄棕壤最高,潮盐土次之,灰潮土最低。2 种处理下的 F_5 百分含量变化与前 4 种形态相反,出现原土硒百分含量远大于外加硒的,成为外加硒处理中的一个明显特征。

通过上述结果分析表明,不管是原土硒还是外加硒,它们在 3 种土壤中诸形态分布具有相似的规律。这表明原土硒和外加硒都同样受到不同土壤性质的影响。结合表 1 土壤性质分析可知,土壤为碱性, pH 值高,土壤硒溶解度就大,土壤硒易被植物吸收利用。反之,若土壤为酸性, pH 值低,土壤硒不易为植物吸收利用。说明土壤 pH 对硒形态分布影响较大。Gissel-Nielsen^[3]1973 年

的研究取得了与本文相一致的结果。笔者对黄棕壤外加硒在伴施 $0.5\% \text{CaCO}_3$ 下的培养试验也发现,加入 CaCO_3 后,引起土壤 pH 的提高,有利于黄棕壤中硒的溶解度增加, F_1 和 F_2 百分含量提高。此外,土壤粘粒及游离氧化铁含量对硒诸形态分布也有一定影响。如潮盐土、灰潮土 2 种土壤,它们的 pH 值分别为 7.80 和 7.75,几乎相同,但外加硒 F_1 、 F_2 的百分含量为灰潮土 > 潮盐土,这一次序与 2 种土壤粘粒及游离氧化铁含量次序相反。另一方面, F_3 、 F_5 百分含量为潮盐土 > 灰潮土,这一次序却与 2 种土壤的粘粒含量及游离氧化铁含量一致。若考虑 3 种土壤外加硒诸形态与粘粒和游离氧化铁含量的关系,亦可得到同样的结果。这可能是由于土壤粘粒及游离氧化铁含量高,对土壤硒的吸持能力增强,致使硒的溶解度、有效性降低。

灰潮土、潮盐土的原土硒诸形态分布与粘粒、游离氧化铁的关系不如外加硒的明显,可能是由于原土硒浓度太低,测试上有一定误差之故。

比较 2 种处理下诸形态百分含量的变化,外加硒 F_1 (黄棕壤例外), F_2 、 F_3 形态硒含量提高较多, F_4 变化小,而 F_5 反而大大降低。说明外加硒在一定时期内(如 4 个月)的有效性较高,也表明外加硒是解决低硒地区土壤缺硒的一种措施。

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(上接第 55 页)组回归方程仅适用于表 3 所列的测定数据范围。为便于实际应用,可据测定数据分段进行直线回归分析,亦可采用曲线回归配合法。

3 结论

水胺硫磷水样在生物降解前后,有机磷、农药含量及降解率与 COD_{Cr} 及其去除率分别呈高度正相关,测定 COD_{Cr} 或 COD_{Cr} 去除率,便可借助

由试验数据建立的回归方程直接导出有机磷与农药的含量或有机磷与农药的降解率。因此,选用 COD_{Cr} 去除率作为固定化微生物对农药降解活性的常用评价指标是适宜的。

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than 0.5 mg/L, i. e., the national standard for its discharge.

Key words: acidic wastewater, pollution control, arsenic (As), iron salts neutralization.

Study on the Manufacture of Activated Carbon from the Carbon in Coal Ash from a Power Station. Wu Xinhua and Yu Wei (Fujian College of Forestry, Nanping 353001); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 47—49

A production process of activated carbon in which the carbon in a coal ash from a power station was used as a starting material has been developed. The optimized conditions for this process to produce a granular activated carbon were using charcoal, white charcoal or coal as an auxiliary raw material, together with which the starting material was undergoing a treatment in a preactivation process, then was washed with acid and water, and finally was activated or even further reactivated if required. The activated carbon product thus produced had an iodine value of 600—700 mg/g. The activated carbon from a pilot industrial production had an iodine value of 630—800 mg/g with a wearability of over 95%. This process provides a new way for coal ash to be utilized comprehensively.

Key words: coal ash, activated carbon, comprehensive utilization.

Comparative Study on the Capacities of Aerobic and Anaerobic Immobilized Microbes to Treat Organics. Wu Xiaolei et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 50—52

Activated and anaerobic sludges were respectively immobilized with polyvinyl alcohol (PVA) used as an entrapping agent, and then the immobilized sludges were separately used to degrade the organics in wastewater under the aerobic and anaerobic conditions, respectively. Comparisons in the capacity of treating organics were also made between the immobilized and free sludges and between the immobilized activated sludge and the immobilized anaerobic sludge. The results show that the volumetric loading was 1.3 to 2.1 times that of free sludge, meant by that the immobilized sludges had a higher capacity of treating organics than a free sludge. Under the conditions studied, the volumetric loading ratio of the immobilized anaerobic sludge to the free anaerobic sludge (2.13) was much higher than that of the immobilized activated sludge to the free activated sludge (1.30—1.54). Considering the sludge loading and gas yield per unit of sludge by weight, it was concluded that the capacity of microbe treating organics could be further developed in the immobilized anaerobic sludge so that the immobilized microbes entrapped in a gel would be more suitable for the anaerobic treatment of a high strength organic wastewater.

Key words: immobilized microbes, immobilized

activated sludge, immobilized anaerobic sludge, treating capacity.

Study on the Indicators for Evaluating the Activity of Immobilized Microorganism in the Degradation of Isocarbophos. Zhang Xiaohe et al. (Institute of Environmental Medicine, Tongji Medical University, Wuhan 430030); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 53—55

The indicators for evaluating the performance of immobilized microorganism before and after the biodegradation of isocarbophos in water samples have been studied. It has been found that the levels and degradation rates of the organophosphorus pesticide in water were in highly positive correlation to COD_{Cr} and COD_{Cr} removal, respectively, so that it would be proper to choose COD_{Cr} removal as a routine indicator for evaluating the activity of immobilized microorganism in the degradation of this pesticide. What was given in this article also included the regression equations established on the basis of experimental data, and the results from their significance tests, wherein the correlative coefficients of Eqs. 1—4, Eqs. 5 and 7, Eqs. 6 and 8, and Eqs. 9—12 were 0.992, 0.940, 0.951 and 0.978, respectively.

Key words: Isocarbophos, immobilized microorganism, biodegradation, indicators for evaluating activity.

Speciation of Selenium in Soils. Lan Yeqing et al. (Dept. of Basic Courses, Nanjing University of Agriculture, Nanjing 210014); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 56—58

The distribution of natural and applied selenium (Se) species in three kinds of soil, i. e., tide-saline soil (C), gray tide-soil (G) and yellow brown soil (Y), in Jiangsu province was studied. The results show that the naturally occurred Se species were mainly distributed as residual species (F_5), and F_5 in each of the three kinds of soil accounted for about 80% of total Se species. After an incubation for 4 months, the applied Se species were relatively homogeneous to be distributed as soluble species (F_1) (except in Y), exchangeable species (F_2), aqueous ammonia extractable species (F_3) and residual species (F_5). With two different treatments, the distribution of Se species was found to be in some relation to soil pH value, glutinous grains and free iron oxide levels. The soil pH value was in such an order as $C \approx G > Y$; the levels of glutinous grain and free iron oxides; $Y > C > G$; the percentage levels of F_1 and F_2 : $C \approx G > Y$; and the percentage levels of F_3 and F_5 : $Y > C > G$.

Key words: selenium (Se), soil, species.

Preliminary Analysis of Design Flow for Allowable Discharge Capacity of Rivers. Zheng Yingming (Institute of Environ. and Water Conservancy, Hehai University, Nanjing 210024); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 59—61