低 pH 值及铝对泥鳅吸收^{45}Ca的影响*

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摘要　为了探讨低 pH 和铝对水生生物的毒性或联合毒性效应，进一步研究钙缓解作用机理，用放射性核素^{45}Ca作为示踪剂，研究在低 pH 值及加铝条件下，泥鳅(*Misgurnus anguillicaudatus*)对钙离子的吸收分布情况. 结果表明，生长在 pH 为 7.10 时，^{45}Ca 在泥鳅体内各器官的 96 h 放射性比度为：皮肤 39532 cpm/g，骨骼 38116 cpm/g，鳃 25495 cpm/g，肌肉 1651 cpm/g；低 pH(4.70)条件下，泥鳅体内^{45}Ca含量较正常条件下(对照组 pH7.0)下降百分比为：皮肤 81.07%，骨骼 84.41%，鳃 80.11%，肌肉 5.88%；在低 pH 值并加铝时，泥鳅体内各器官^{45}Ca含量与对照组相比，下降百分比分别为：皮肤 89.87%，骨骼 88.83%，鳃 86.17%，肌肉 26.47%. 并讨论了酸雨危害对鱼体钙代谢的可能影响.

关键词　低 pH，铝，钙，泥鳅，吸收.

有研究表明，环境中铝钙离子的比例，对铝的生物毒理作用具有一定的调节作用. 金洪均等对不同铝钙离子比及不同 pH 值条件下铝对鱼类的生态毒理学研究认为，钙的加入有利于缓解低 pH 值和铝对水生生物的毒性[1]. 关于钙缓解酸性 pH 及铝的毒性作用机理，仍在探讨中. 本研究以泥鳅作为试验生物，用放射性核素^{45}Ca作为示踪剂，研究不同 pH 条件下铝离子的存在对泥鳅吸收环境中钙离子功能的影响，以探讨低 pH 及铝对水生生物的毒性或联合毒性效应，以便更深入研究钙缓解作用机理.

1　材料与方法

1.1　生物及培养方法

泥鳅(*Misgurnus anguillicaudatus* Cantor)平均体长为 15.6±1cm，体重 16.5±2.5 g，由南京市养鱼场提供. 实验前，在实验室内水池中驯养 1 周后进行实验. 实验容器为玻璃缸(40L)，用水为自然曝气 3 d，并用活性炭过滤脱氯的自来水，温度 21±1℃，电导 190±30 μs/cm，pH 7.50±0.30，DO 5.2±0.2 mg/L，硬度($CaCO_3$ 计)115.0±8.0 mg/L.

1.2　溶液 pH 值及铝浓度处理方法

设立 1 个对照组(A)和 2 个处理组(B、C). 各实验组 pH 值及 Al 浓度参考文献[2]等设定. 对照组中水的 pH 值为 7.10±0.30；处理组 B、C 组中水的 pH 值为 4.70±0.30，处理组 C 中并加入 $Al(SO_4)_3$，使其最终 Al 离子浓度为 1.0 mg/L. 在实验期间，每天用 S-3A 型 pH 计测定水样的 pH 值 2 次，并用 0.5 mol/L 硫酸校正.

1.3　^{45}Ca 的加入及测定

实验开始时，加入$^{45}CaCl$，使每个实验组中水样的放射性比度为 5000±200 cpm/ml，然后每个实验组(8 个水族缸/组)中共放入泥鳅 16 尾，于 1、5、15、24、48、64、72 和 96h 在对照组及 2 个处理组中各取 2 尾泥鳅，先后用自来水及蒸馏水多次冲洗，并取鳃、皮肤、肌肉、脊锥骨等样品，每份为 50 mg，放入闪烁瓶内，加 0.2 ml 甲酸，0.4 ml 30% H_2O_2，加盖，水浴加热消化，75℃，1—2 h，期间摇动样品 3—4 次，使组织块分解并易消化，待各器官消化成液体后，取出在室温下冷却，放置过夜. 测定前，各样品中加入 3 ml 乙二醇乙醚，轻轻振荡，再加

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入 3 ml 甲苯闪烁液，待溶液透明清澈后，在 Beckman LS-9800 型液体闪烁计数仪上测定并计算放射性比度 cpm/g 值，测定环境温度为 25℃，湿度为 65%[3]. 所用放射性元素由中国科学院原子能研究所提供，每个样品测定设 4 个平行，并重复实验. 实验数据用 STATG 统计软件包进行统计分析.

2 结果与讨论

2.1 酸性 pH 值及铝对泥鳅吸收钙离子的影响

随着暴露时间延长，不同处理组中泥鳅各器官对^{45}Ca的吸收及积累见图 1. 除肌肉样品在各实验组中钙离子含量几乎没有变化外，不同 pH 值以及铝离子的存在，对泥鳅的皮肤、鳃、骨骼等器官中^{45}Ca 的吸收均有明显的影响.

在 pH 为 7.10 的对照组中，当暴露于^{45}Ca中近 48h，泥鳅皮肤中的^{45}Ca 含量达到本实验的最大值，放射性比度达到 56500 cpm/g，随着暴露时间的延长，鳃和骨骼中的含量也明显有所增加；当水体的 pH 值下降到 4.70 时，虽然各器官对水中^{45}Ca的吸收作用随着暴露时间的延长，有所加强，48 h 后，也可达到一峰值，但在各器官中的积累量明显低于对照组；在同样暴露时间后，泥鳅皮肤中放射性比度仅为 20000 cpm/g，与对照组相比，下降了 65%；当暴露于酸性 pH，并有铝离子存在时，泥鳅各器官对^{45}Ca 的积累更低，同样的暴露时间，皮肤中^{45}Ca含量仅为对照组中的 7%，其它器官中^{45}Ca 积累量也呈显同样的趋势，几乎没有明显的峰值. 这个实验结果表明，酸性 pH 抑制了泥鳅对环境中钙离子的吸收和积累，而铝离子的存在，与酸性 pH 起着联合作用，对各器官的钙离子吸收及积累有着更明显的抑制作用. 不同处理条件下泥鳅体内^{45}Ca 含量的顺序为 pH7.10＞pH 4.70＞pH4.70＋Al，配对数据 t 检验，2 种处理与对照组均有显著差异($a=0.05$).

低 pH 条件下，由于环境中H^+离子浓度升高，使得体内外电位平衡发生移动，钙离子从体外向体内主动运输受到抑制，从而鳃和皮肤对钙离子的吸收减弱. Joseph 等人[4]在研究低

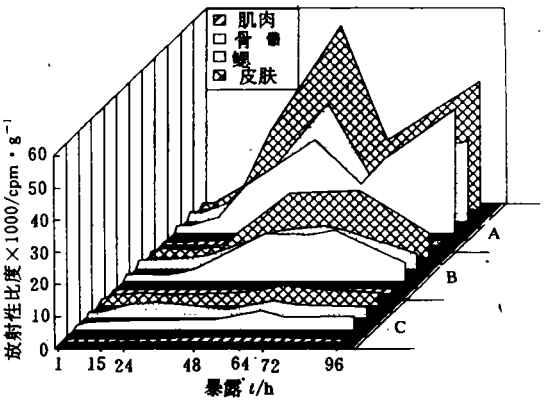

图 1 不同处理条件下泥鳅各器官中放射性比度随时间变化关系

A. pH 7.0 B. pH 4.7 C. pH 4.7＋Al(1.0 mg/L)

pH 及铝对鳟鱼发育影响时，曾经观察到，当处理的水体中没有铝离子存在时，溶液中的钙离子浓度相对较低，对此，他们当时未能明确其原因，但提出了一种假设：即有可能当暴露于 pH 7.5 时，鳟鱼从水体中对钙离子的吸收效率要高于有铝离子存在时的效率. Spry[5]的实验表明当鱼暴露于高锌时，完全抑制了鱼鳃对钙离子的吸收，导致了钙离子原生质化速率的明显下降，他们也提出了类似的假设：如果铝离子有与锌同样的效果，那么，当有铝离子存在时，将会抑制鱼对钙离子的吸收. 本实验通过对暴露于不同 pH 及加铝后鱼体内各器官中^{45}Ca 浓度的比较研究，进一步证实了 Joseph 及 Spry 等人的假设.

Helge[5]的野外调查显示，湖泊酸化后，白胭脂鱼骨骼中钙含量明显降低，考虑到钙在鱼类生长过程中的生理作用，他们提出了在酸性水中鱼体内正常钙代谢失调的论点. 他们的实验也证明，在用 pH 为 4.0 的水处理鳟鱼时，当钙离子达到一定浓度，即能提高鱼的存活率，这进一步说明了钙离子在鱼生存中的重要性.

2.2 不同器官对钙离子积累差异的比较

在比较各器官对^{45}Ca积累的情况时可以看出，在不同处理组中，各器官中^{45}Ca 的积累峰值出现的时间基本一致，在 48—72h 之间. 但不同器官内钙离子的积累量却相差甚远. 实验开始时，各器官内^{45}Ca 的含量均在 1800 cpm/g 左

右. 暴露 1—24 h 后，皮肤中的^{45}Ca含量高于其它器官，直至 48 h 达到峰值，其次为鳃. 各器官中^{45}Ca的含量顺序为：皮肤＞鳃＞骨骼＞肌肉；在峰值出现后，各器官中^{45}Ca积累量逐步下降，而不同器官内的^{45}Ca含量顺序并无变化，并维持至实验末期(96 h). 在这一段时间中，各器官中的^{45}Ca在对照组中，在经过波动后，又逐步上升，再次达到一定水平；在 B、C 处理组中则继续呈下降趋势，直至实验结束. 比较 96h 放射性比度，可以看到，在低 pH(4.8—5.3)条件下，泥鳅体内^{45}Ca含量较对照组下降百分比分别为：皮肤 82.07%，骨骼 85.27%，鳃 80.11%，肌肉 24.05%；在低 pH 并加铝处理中，泥鳅体内各器官^{45}Ca含量的下降百分比分别为：皮肤 90.28%，骨骼 89.06%，鳃 87.17%，肌肉 15.47%. Terry 等人[7]对湖水酸化影响各种金属元素(锌、铝、镉和铅)在鱼体不同器官中积累研究结果，也得到类似的结论.

在本实验中，皮肤中^{45}Ca的含量之所以最高，可能是由于泥鳅皮肤表面附着的鳞片积累了大量的钙，虽然在测定放射性比度前预处理时，曾经过反复冲洗，但附着量仍然高于其它器官；酸性 pH 和铝对鱼类的毒性机理研究表明，鱼鳃是受害的靶器官，低 pH 首先影响的是鱼鳃. 本实验中，在低 pH 及加铝处理组中，观察到鱼鳃部有白色粘液积累，鳃片受到损伤，这种可见伤害可能是由于铝离子沉积在鳃的表面，引起鳃片阻塞，削弱了鳃的离子交换能力及呼吸功能，导致渗透压调节机制失控. 金洪均等人的电镜观察也表明，鱼类暴露于 pH 4.5 条件下 8 h，鳃组织已受到严重损伤，尤其是鱼鳃表面行主动吸收功能的特化上皮细胞明显坏死[1]. 在低 pH 及加铝处理后，骨骼中的^{45}Ca含量下降百分比较高(88%)，这与骨骼本身对钙离子的吸收特点以及骨钙与血钙的平衡机制有关. 一般情况下，骨骼具有较大缓冲容量，成为鱼体的钙库，从生理上来说，骨骼中的钙离子含量一旦下降，难以在短时间内恢复到正常水平，而且对鱼体的代谢及生长所产生的潜在危害也最大. 与其它器官相比较，肌肉内的钙含量无论是本底值还是暴露于低 pH 和加铝条件下，其积累量都是最低水平，低 pH 及加铝处理对其影响也不大.

从本实验比较各处理组中不同器官^{45}Ca吸收受影响程度，可以看出，在不同时间的样品中，尽管不同器官中^{45}Ca含量绝对值有明显的差异，但其波动趋势比较一致，这可能是由于皮肤及鳃具有从体外直接吸收钙的能力，而鳃在受到严重损伤，吸收机制遭到破坏后，泥鳅体内钙的总体水平下降. 骨骼则是主要从体内积累储存钙. 所以，低 pH 及加铝直接削弱了泥鳅从体外吸收钙的能力. 当然对钙的积累也受到抑制，这又影响了体内钙离子的代谢和转化，进而导致了骨骼中钙离子含量的剧烈下降.

3　结论

(1) 在低 pH(4.70)条件下，泥鳅对钙离子(^{45}Ca)的吸收积累受到明显的抑制，低 pH 与低浓度的铝(lmg/L)具有联合毒性作用，进一步降低了泥鳅对环境中^{45}Ca的吸收，泥鳅体内^{45}Ca含量从高到低的顺序为 pH7.10 ＞ pH4.70 ＞ pH4.70＋Al；

(2) 在不同处理组中，各器官内^{45}Ca含量顺序为：皮肤＞鳃＞骨骼＞肌肉，而低 pH 及加铝对鳃片作用产生了可见伤害，对骨骼中^{45}Ca含量的下降影响较为明显；

(3) 从生理学意义上来看，水体酸化对鱼类及水生生态系统产生的作用机理之一可能是水体的低 pH 及铝离子存在，导致鱼类及其它水生生物体内钙代谢失调.

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creasing with reaction time under conditions of 0.85 MPa and 900℃, and the conversion rate is in range of 23.5% to 42% at 120 minutes. The conversion rate is drastically growing with temperature under conditions of 1.15 MPa and 750—950℃ at 120 minutes. The conversion rate was slowly and linearly increasing with pressure under condition of 860℃. Finally, the reaction mechanism was discussed.

Key words: pressurized thermogravimetric analysis, limestone, dolomite, desulfurization.

Study on the Regeneration of $NaHSO_3$ in the Recovery of SO_2 from Flue Gas by Bipolar Membrane Electrodialysis. Yu Lixin et al. (Department of Chemical Engineering, Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 40—42

Bipolar membrane electrodialysis is adopted in the regeneration of $NaHSO_3$, which is used as absorbent of SO_2 from flue gas. When cation-exchange membrane is supplemented with , both homogeneous and heterogeneous bipolar membranes which are made in our lab and by Shanghai Chemical Factory, respectively, can produce satisfactory conversion ratio (higher than 80%) in the regeneration process. The decrease of current efficiency (from approximately 80% to approximately 20%) is resulted from the increase of the concentration of proton in acid chamber. The existence of small amount of Na_2SO_4 in $NaHSO_3$ solution doesn't cause much effect on regeneration process. The short membrane lifetime hinders the process from getting into practical application.

Key words: bipolar membrane electrodialysis, recovery of SO_2 from flue gas, regeneration of $NaHSO_3$.

Study on Characterization of Adsorption of Zine onto five types of soil in Beijing Area. Zhou Wei and Li Jiyun (Research Center for Eco-Enviromental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 43—45

The results of study on adsorption of zine onto five types of soil in Beijing area showed that the capacity of five types of soil adsorbing zine presents positive correlation with pH volue of the soil solution, contents of organism and $CaCO_3$ etc in soil. The adsorption data could be fitted to the Freundlich-type equation.

Key words: adsorption, zine, soil, Beijing area.

A Study on Acclimation Technique of Activated sludge and Biological Treatment of High Consistence Cheni-thermomechanical Pulp Wastewater. Chen Min (Guangdong University of Technology, Environment & Resource Engineering Department, Guangzhou, 510090), Sung-Nien Lo and H-Claude Lavallée (Université du Québec à Trois-Rivières, Québec, Canada, G9A 5H7): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 46—49

The treatment of high consistence Cheni-thermomechanical Pulp (CTMP) pulping wasterwater using activated sludge method was studied in this paper. The effect of improving technique in activated sludge acclimation on the sludge settleability and removal efficiencies was discussed. The Experiments showed that the improved technique i. e combination of batch and continous feed in sludge acclimation process can remarkably improve the sludge settleability and removal efficiencies. The sludge volume after 30 minutes of settling was 290—320 ml/L, sludge volume index was 48—55 ml/g, the removal of COD reached to 77%—85%, removal of BOD_5 was 90%—95%, removal of TSS was 75%—89%.

Key words: batch feed, continous feed, activated sludge, acclimation technique, CTMP wastewater.

Test of Tar Emulsified Liquid as Dust Suppressant for Dirt Roads. Wu Chao et al. (Dept. of Resources Exploitation Engineering, Central South University of Technology, Changsha 410083): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 50—52

In order to control the dust raising on the dirt roads efficiently, the tar emulsified liquid with low concentration was taken as the dust suppressant. Based on a great number of experiments in laboratory, the optimum compositions of surfactants and the prepared condition for emulsifying tar were achieved, tar is 3%—6%, surfactants is 0.5% and water is 93.5%—96.5 Wt. %. The prepared temperature is greater than 70℃. Depended on a lot of tests both in laboratory and field, the results showed that the liquid is very efficient for binding dust and maintaining the dirt roads. The active time can reach more than 10 days, when the liquid is sprinkled on the road in 2.2 kg/m^2. A rational profit can also be achieved after it is used for years.

Key words: dust suppressant for roadway, tar emulsified liquid, field test.

Electrochemical Separation Process for Recovery of Gold, Silver and Lead from Scrap. Liang Huqi et al. (Dept. of Chem. Eng., Shanghai University, 200072): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 53—56

The electrochemical separation process for comprehensive recovery of gold, silver and lead from Au, Ag-containing scrap was investigated. The smooth and dense cathodic deposit with purity of 99% Pb was prepared by electrochemical separation process under the optimum technological conditions (electrolyte composition: 70 g/L Pb^{2+}, 100 g/L total SiF_6^{2-}; solution temperature: 40 C. current density: 100 A/m^2; concentration of β-naphthol tobone glue: 0.002 g/L and 0.5 g/L) experimentlly. The current efficiency of lead was higher than 98%, the specific electric energy consumption was 117 kW · h/tPb. The recovery of Au and Ag in the anode slime were as high as 99% and 98% respectively.

Key words: recovery of Au and Ag, electroche mical separation, treatment of scrap.

Effects of Low pH Value and Aluminum on Uptake of ^{45}Ca by *Misgurnus anguillicaudatus*. Kong Fanxiang et al. (Dept. of Environ. Sci. and Eng., Nanjing University, Nanjing 210093): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 57—59

The effects of low pH value and with or without the addition of aluminum on the uptake of ^{45}Ca by *Misgurnus anguillicaudatus* were studied. The results showed that

the specific activities of ^{45}Ca are 39 532 cpm/g in skin, 38 116 cpm/g in skeleton, 25 495 cpm/g in gill and 1 651 cpm/g in muscle respectively after exposed to pH 7. 10 (control) for 96 h. Compared with the control, the specific activities of ^{45}Ca decline about 81. 07% in skin, 84. 41% in skeleton, 80. 11 % in gill and 5. 88 % in muscle after exposed to pH 4. 70 without aluminum. Under the condition of pH 4. 70 with the addition of aluminum (1. 0 mg/L), the specific activities of ^{45}Ca decline about 89. 87% in skin, 88. 83% in skeleton, 86. 17 % in gill and 26. 47 % in muscle respectively. The effects of acid rain on the calcium metabolism in fish were discussed.

Key words: low pH, aluminum, ^{45}Ca, uptake, *Misgurnus anguillicaudatus*.

The Removal of Some Organic Pollutants in Rapid Infiltration Treatment System of Waste Water. Wu Yongfeng et al. (China University of Geosciences, Environmental Science Department, Beijing, 100083): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 60—62

The removal of some organic pollutants trichloromethane, tetrachloromethane, trichlorothylene, benzene and toluene in rapid infiltration treatment system of waste water have been simulated in large scale soil colums. The three kinds of chlorinated aliphatic hydrocarbons were rapidly removed from influent concentration of 2000—6000 μg/L to effluent concentration of less than 100 μg/L. The removal effects of benzene and toluene depended on the flooding time. In the early part of flooding period, benzene and toluene could be removed rapidly from influent concentration of 1000—1700 μg/L to effluent concentration of less than 100 μg/L. With the increase of flooding time, the removal effect became lower and lower until the effluent concentration of benzene and toluene almost equal to the influent concentration.

Key words: rapid infiltration, chlorinated aliphatic hydrocarbons, aromatic hydrocarbons smulated test.

Study on the Treatment of Wastewater from the Production Processes of Vitamin B_{12} and Starch by Using UASB Reactor. Yang Jingliang et al. (Dept. of Environ. Eng., Hebei Institute of Chemical Technology and Light Industry, Shi jiazhuang 050018): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 63—65

In Order to research the feasibility of treating wastewater from the production processes of vitamin B_{12} and starch by anaerobic process, the study on treating the wastewater by UASB reactor was made. The results indicated that the volumetric loading of COD was 30 kg/(m^3·d), removal rate of COD was 80% and volumetric producing gas rate was 16. 80 m^3/(m^3·d) when influent concentration of COD was 10^4—1. 2×10^4 mg/L.

Key words: upflow anaerobic sludge blanket reactor, mixed wastewater of vitamin B_{12} and starch.

Spectrophotometric Method for the Simultaneous Determination of Phenols and Aromatic Amines in Sewage with 4-AAP. Li Meirong and Yuan Cunguang et al. (Dept. of Chemical Enginee ring, University of Petroleum, Shandong, 257062): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 66—68

A modified spectrophotometric method of determination for phenols and aromatic amines of sewage was discribed. It was found that the peak ranges of phenols were 500—540 nm and that of aromatic amines were 530—480 nm using 4-aminoantipyrine (4-AAP) with potassium hexacyanoferrate and ammonium peroxydisulfate in the medium of pH 5. 5 HCl-$(CH_2)_6N_4$. Phenols of 0. 1—30 mg/L and aromtic amines of 0. 008—3. 0 mg/L were determined simulaneously by spectrophotometry without predistillation and extraction. Lower than that 0. 3 mg/L of sulphide and co-oil in sewage have no interference with determination of phenols and aromatic amines. The interference of Cu^{2+} and Fe^{3+} could be removed by EDTA masking. The recovery for phenols and aromatic amines were 98%—105% and 95%—105%, respectively. The sensitivies samples of 10 phenols and 13 aromatic amines were studied.

Key words: spectrophotometry, 4-aminoantipyrine, phenols, aromatic amines.

Pretreatment and Detection of Organophosphorus Pesticide Residue in Environmental Sample. Liu Feng et al. (Institute of Environmental Science of Suzhou, 215004): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 69—70

Detection of methamidophos, dimethoate and parathion-methyl pesticide residue by FPD, NPD and ECD can be accurately determined. Extraction of solid sample into methanol aqueous solution solvent and direct aqueous solution injection not only simplify pretreatment steps but also with enough accuracy. Addition standard recovery rate of soil samples was in range of 93%—98%. The detection limits of dimethoate in water sample were 0. 05 mg/L for FPD, 0. 001 mg/L for NPD and 0. 002 mg/L for ECD, respectively.

Key words: organophosphorus pesticide residue, methanol aqueous solution, direct aqueous solution injection, determination.

Study on the Overall Control Plan of SO_2 Emission from. Small and Mid-scale Coal Combustors in Liuzhou City. Xu Kangfu et al. (Dept. of Environ Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **17**(6), 1996, pp. 71—73

Toward the SO_2 emission control technology developed in China for small and mid-scale coal combustors, a research was carried out on the technology perfection and cost-effectiveness analysis, and a practical overall plan for SO_2 emission abatement in Liuzhou city was presented. This plan can ensure the fitness of briquette combustion-rent sulfur and fluidized-bed combustion desulfurization by means of mixing for the high sulfur content low heating value coal and can improve the depth of desulfurization by utilizing the excessive base material and innovating the current wet collection device.

Key words: coal-combustion pollution, SO_2 emission control, desulphurization cost, desulphurizatioen overall control plan.