饮水除氟剂的试验评估

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摘要　就聚合铝，CF-1 和 PC85-3 除氟的适宜条件，如 pH，陈化作用，搅拌等进行了较详细的比较。聚合氯化铝除氟的最佳 pH 为 6—7；水温在 10—30℃，除氟效果基本相近；搅拌时间以 1—3min 为宜；沉淀静置 10—15min 能达到除氟要求。并对活性氧化铝，骨炭和 UR-3700 螯合树脂除氟的平衡容量，水的硬度影响等进行了试验。结果表明，聚合铝，CF-1 和 PC85-3 去除饮水中的过量氟，可达到饮用要求，但其应用受限制。活性氧化铝，骨炭是比较有效的除氟滤料，活性氧化铝平衡吸氟量为 0.89—1.75mg/g，除氟效率与 pH、原水含氟量、盐度和硬度有关。

关键词　除氟，聚合铝，活性氧化铝，骨炭，饮水。

我国约有 7700 万人口深受饮用高氟水的危害。饮水除氟的方法主要有混凝沉淀、滤层吸附、电凝聚、电渗析、反渗透等。在混凝沉淀法和滤层吸附法除氟过程中，除氟药剂和滤料的除氟性能，产品质量，以及适宜的运行使用条件是达到除氟效果的关键。饮水除氟剂的种类繁多，除氟效果有很大差异。本文目的是从有较好除氟效果，并得到一定实际应用的除氟剂中选取有代表性的除氟剂，对其除氟效果和运行使用条件进行检验，为除氟剂的研究推广应用提供参考。

1　试验材料

1.1　除氟药剂

(1)聚合氯化铝　分子式$[Al_2(OH)_nCl_{6-n}]_m$，淡黄色固体(简称 PAC)。

(2)CF-1 型饮水除氟剂　白色微黄的粉粒固体。

(3)PC85-3 型除氟剂　一种以铝盐为主要成分的铝系化学除氟剂，黄色固体粉末，易潮解。

1.2　除氟滤料

(1)活性氧化铝(AA313 型)　比表面积≥200m²/g，白色球状颗粒，粒度 2—3mm。

(2)BC 型除氟剂　主要成分为羟基磷酸钙$[Ca_{10}(PO_4)_6(OH)_2]$，比表面积 90m²/g，粒度 20—55 目，吸附容量 3.0—3.5mg(F)/g-BC。

(3)UR-3700 螯合树脂　一种氧化锆的氢型螯合树脂，棕色球形颗粒，粒度 20—60 目。

1.3　其它试剂

NaF、NaOH、$Al_2(SO_4)_3$ 等试剂为分析纯或优级纯。

2　主要仪器设备

(1)pHS-3C 型酸度计(上海雷磁仪器厂)。

(2)Orion SA720 离子计　氟离子选择电极。

(3)8391-37 型浊度计(美国 Cole-Parmer 仪器公司)。

(4)电感耦合等离子体发射光谱仪(美国，Jarrell-Ash 1155V 型)。

(5)MW-D 型摇床(日本宫本理研工业株式会社)。

(6)磁力搅拌器(CJ 型，河北新城机电工业公司)。

3　除氟药剂的除氟效果试验

3.1　一般操作步骤

取用自来水配制的含氟水 500ml 或 1000ml，盛于烧杯内，投加除氟剂后，搅拌 2min，自然沉降 20—60min 后测定其水中的氟含量、pH 值及其它水质参数。水中的氟含量用离子选择电极法测定[1]。

3.2　有关条件影响的试验结果

3.2.1　除氟效果与 pH 关系

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原水含氟量 6.39mg/L，用 0.1mol/L HCl 或 0.1mol/L NaOH 溶液调节 pH 值。除氟效果与 pH 关系如图 1、2 所示。

图 1、2 结果表明，原水的 pH 对除氟效果影响较大，这 3 种除氟剂的适宜 pH 值范围基本相同。PAC 除氟的最佳 pH 值在 6—7 之间[2]。

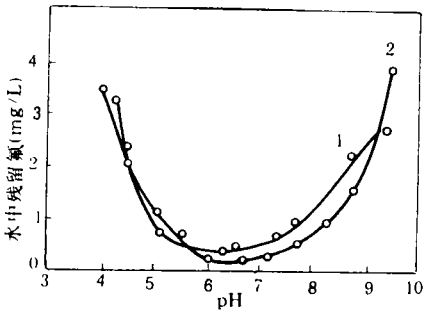

图 1 水中残留氟量与 pH 关系
1. CF-1 2. PAC

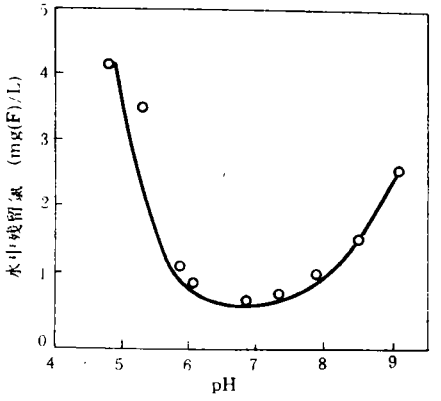

图 2 PC85-3 的 pH 与水中残留氟量关系

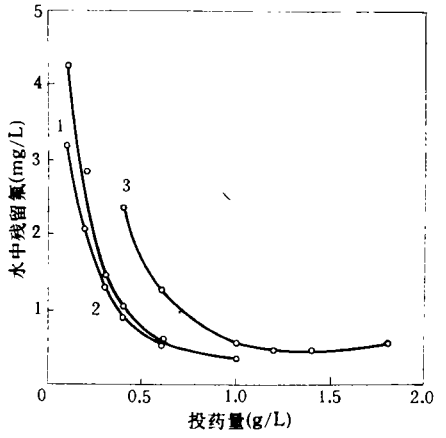

图 3 除氟剂投加量与水中余氟量关系
1. PAC 2. CF-1 3. PC85-3

3.2.2 除氟效果与投药量的关系

除氟剂的投加量与水的含氟量、pH、水质等因素有关。原水含氟量为 4.4mg/L，pH=8.0，碱度 2.8—3.0mmol/L。除氟剂的投加量与水的余氟量关系如图 3 所示。

3.2.3 除氟效果与水温变化关系

水温与除氟剂的除氟容量关系试验表明，水温在 10—30℃，除氟效果基本相近。用铝盐系除氟剂对高氟水除氟时，水温是混凝反应中的一个重要因素。如温度过高，氢氧化铝的水合作用增强，沉淀下沉慢，甚至漂于水面，影响除氟效果。

3.2.4 除氟效果与搅拌时间关系

取含氟量 3.87mg/L 原水，加入适宜量除氟剂，以转速约 120r/min 搅拌机搅拌不同时间，放置后测水中残留氟量。结果表明，搅拌时间以 1—3min 为宜。搅拌时间过长，除氟效果不好[3]。

3.2.5 除氟效果与沉淀放置时间关系

向含氟量 3.87mg/L 原水中加入适量除氟剂，放置 10min 至 72h 进行观测。结果表明，加入除氟剂沉淀静置 10—15min 即能达到除氟要求，沉淀放置 15min—72h 内，除氟效果无明显变化。沉渣在水中浸泡 72h，不会向水中释放氟离子[4]。

3.3 除氟后的水质分析

每组取 5—11 份各 1L 原水，分别投入 0.6gCF-1 或 PAC，1.4g PC85-3，处理后的水质按常规方法测定 pH、浊度、总硬度、Cl^-、SO_4^{2-}、F^- 等项目，以电感耦合等离子体发射光谱法测定水中 23 种元素含量。CF-1 和 PAC 除氟后的水质符合《生活饮用水卫生标准》。CF-1 除氟后水中的氯化物和硫酸根略有增加。PAC 除氟后的水中氯离子也有所增加[3]。PC85-3 除氯后的水质除氯离子浓度 294mg/L 超标准(250mg/L)外，其它检测项目均符合国家饮水卫生标准。处理水中氯离子超标，其原因是除氟剂中含有可溶性氯化物较高。因此，在除氟剂生产过程中应减少或限制氯化物含量。

4 除氟滤料的除氟效果试验

4.1 试验方法

4.1.1 含氟水样

试验中使用的含氟水样，在自来水中加入一定量的氟化钠，待溶解搅拌均匀后，用氟离子选择电极法测定其准确含量。

4.1.2 滤料预处理和再生

除氟滤料须进行预处理，待除氟剂饱和后须再生处理。活性氧化铝用2%硫酸铝溶液，BC除氟剂用1%NaOH溶液浸泡过夜并用0.05mol/L H_2SO_4 中和，然后均用蒸馏水洗至中性。螯合树脂先用2倍于树脂体积的2mol/L NaOH溶液浸泡，水冲洗，再用2倍于树脂体积的1mol/L HCl浸泡，最后用水冲洗至中性。取上述除氟滤料10.0g装填至直径10mm玻璃柱内，通过含氟水，流速0.5—2.0ml/min，待出水含氟量超过1.0mg/L时，按滤料预处理方法进行再生后才能继续使用。

4.2 有关条件影响试验结果

4.2.1 除氟滤料的平衡吸附量

原水体积500ml，pH=8.0，水温15℃，除氟滤料各2g，在摇床上振荡3h，静置2h，测定水样含氟量，结果列于表1。活性氧化铝的平衡吸附量结果与资料报道基本一致[5]。BC的平衡吸附量为0.77—1.3mg(F)/g BC。

表1 除氟滤料的平衡吸氟量

原水氟浓度 (mg/L)	Al_2O_3		BC	
	平衡浓度 (mg/L)	平衡吸氟量 (mg/g)	平衡浓度 (mg/L)	平衡吸氟量 (mg/g)
4.35	0.811	0.89	1.29	0.77
10.41	3.42	1.75	5.20	1.30

4.2.2 除氟效果与pH关系

原水含氟量10.4mg/L，水温11—12℃，体积100ml，除氟滤料2g，用0.1mol/L HCl和0.1mol/L NaOH溶液调节pH值，每次搅拌2min，每隔10min搅拌1次，间歇搅拌2h，静置3h，分析水样的残余氟含量，结果如图4所示。

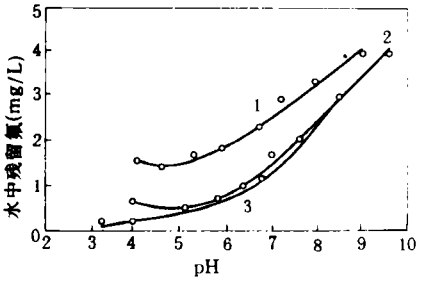

图4 水中余氟与pH关系

1. Al_2O_3　2. BC　3. UR-3700

从图4可见，3种除氟滤料的除氟能力与pH有密切关系。pH值降低，除氟效率均显著提高(残留氟含量明显下降)。以活性氧化铝作除氟滤料，预先调节含氟水pH值，有利于除过量的氟。活性氧化铝的吸氟容量，pH=5.2—5.7比pH=7.0—7.4时高约5倍[6]。在除氟工艺中，采用0.1mol/L H_2SO_4 降低原水pH6.0—6.5，可提高活性氧化铝的吸附容量，减少再生次数，降低出水成本[7]。

4.2.3 除氟效率与原水含氟量关系

原水氟浓度2.0、4.0、6.0、8.0、10.0mg/L，水温10—11℃，pH=8.0，体积100ml，各加2g活性氧化铝或BC，1g UR-3700，间隙搅拌2h，放置2h，测水中残留氟量。除氟滤料的除氟容量与原水氟浓度关系如图5所示。从图5可见，在水质相同条件下，含氟量越高，这3种除氟滤料的除氟容量越大[6-8]。活性氧化铝和BC除氟，适用于高氟水处理。BC除氟工艺已成功地用于山东省高密县大栏乡含氟量高达8.7mg/L的水处理工程。活性氧化铝除氟工艺适用于含氟量<12mg/

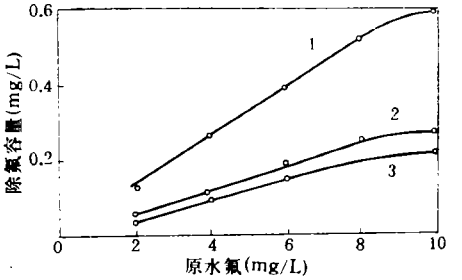

图5 除氟容量与原水氟含量关系

1. UR-3700　2. BC　3. Al_2O_3

L的原水处理[9]。大小粒度活性氧化铝除氟装置在天津市塘沽区和河北廊坊已得到应用[10]。

4.2.4 除氟效率与盐度关系

以含钠量200—600mg(Na^+)/L的原水(以NaCl形式加入)进行试验。原水含氟量4.0mg/L,温度10—11℃,pH=8.0,体积100ml,加活性氧化铝或BC 2g,UR-3700 1g,间隙搅拌2h,放置1h,测定水中残余氟含量。结果表明,原水含盐(Na^+)高达600mg/L情况下,对BC,活性氧化铝的除氟效果没有明显影响,说明这2种除氟滤料对氟离子的选择吸附性高。UR-3700的水中余氟浓度随原水含盐量增加而略有升高趋势,表明盐度对其吸氟效率有些影响。

4.2.5 除氟效率与硬度关系

以硬度为100—600mg/L(以$CaCO_3$计,以$CaCl_2$形式加入)进行试验。原水含氟量4.0mg/L,体积100ml,Al_2O_3,BC各2g,UR-3700加1g,间隙搅拌2h,放置2h,测水中残余氟浓度。结果表明总硬度达600mg/L,对Al_2O_3和BC的除氟效率没有明显变化,而UR-3700的除氟效率随总硬度增加稍有所降低。

4.3 通水试验

除氟滤料经重复使用。3种除氟滤料的试验结果列于表2。

4.4 除氟后的水质分析

上述3种除氟滤料处理的水质经检测,各项指标均符合《生活饮用水卫生标准》。BC除氟滤料处理前后的水质,含氟量从4.4mg/L降至<1.0mg/L,硬度略有降低,其余检测项目无明显变化。活性氧化铝处理的水质基本无变化。UR-3700树脂处理水的总硬度(以$CaCO_3$计)从144.2mg/L降至28.5mg/L。结果说明,这3种除氟滤料均有明显除氟能力,是较好的除氟材料。

表2 除氟滤料除氟试验结果

原水氟浓度(mg/L)	除氟滤料	流速(ml/min)	处理水(ml)	含氟浓度(mg/L)	除氟容量(mg/g)
4.0	Al_2O_3	2.0	2500	0.52—1.0	0.83
4.4	Al_2O_3	1.5—2.0	2500	0.36—1.0	0.92
4.4	Al_2O_3	0.5—2.0	4000	0.30—1.0	1.52
4.4	BC	1.6—2.0	3700	0.04—0.98	1.45
4.4	UR-3700	1.4—2.0	2000	0.13—1.0	0.61
4.4	UR-3700	1.2—2.0	1630	0.30—0.98	0.65
4.4	UR-3700	2.0	1650	0.1—1.0	0.66

5 结论

(1)PAC,CF-1和PC85-3对饮水除氟有较好效果,处理后的水质基本符合《生活饮用水卫生标准》。

(2)PC85-3和CF-1除氟剂的酸度较高。当原水的碱度不足时,需加碱液调节pH值。

(3)活性氧化铝,BC和UR-3700对高氟水的除氟效果良好,处理后的水质没有明显变化,无二次污染。国内BC的价格比活性氧化铝便宜,但BC的机械强度一般较差,运行损耗较大。

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Abstracts

New Progress in Environmental Strategy. Mao Wen'yong (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 1—4

The new progresses in environmental strategy since the 1980s were discussed, which were characterized by the following aspects: (1) Environmental strategy has been expanded to cover the fields of socioeconomic development, forming a new strategy for environment and development; (2) Priority of environmental strategy has shifted from pollution control to ecosystems and resources conservation; (3) Measures for pollution control have changed from the end-of-pipe treatment of wastes to cleaner production, including the production of green products; (4) One of the primary approaches to ecological and environmental conservation has been found to be developing economy while eliminating poverty; and (5) The national strategy of a developing country for environment and development should be in combination with the global environmental strategy while taking international cooperation into account. The future environmental strategy of China, expressed by the China's Agenda 21, has been also described.

Key words: environmental strategy, pollution control, ecological conservation, cleaner production, China's Agenda 21.

Study on the Industrial Ecological Engineering in the Emei Semiconductor Materials Factory. Zhang Yizhang (Emei Semiconductor Materials Factory, Sichuan Province 614200), Chen Lujun (Dept. of Environ, Eng., Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 5—8

A study on the industrial ecological engineering (IEE) was conducted in the Emei Semiconductor Materials Factory by applying the fundamentals of ecology and the methodology of systems engineering and by following the ecological engineerings principles of integration, coordination, circulation and regeneration. The design, implementatiion and evaluation of IEE were also carried out, including the perfection of production chains and the conversion of industrial and domestic wastes to resources. The basic theories on IEE were also described in more details based on the analysis of ecological structures in industries. The results show that the realization of IEE allowed the resources and energy being most efficiently used in the factory, reducing the discharge of pollutants that in turn decreased the damage of industrial production to human beings, thus really achieving the unification of social, economic and environmental benefits.

Key words: ecological engineering (eco-engineering), industrial eco-engineering (IEE), cleaner production, pollution control.

Study on the Inhibition of Mixed Heavy Metals to Anaerobic Digestion. Wang Jusi, Zhao Lihui et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085), Wang Zhenglan et al. (Beijing Institute of Solar Energy); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 9—13

The inhibition of mixed heavy metals (copper, zinc, nickel and chromium) to the anaerobic system in a digester, and the relationship between the concentration of heavy metals daily added and the degree of their inhibition were studied. No inhibition was found when the daily addition of mixed heavy metals was less than 20 mg/L. The digestion system was slightly inhibited when the daily addition was 20—30 mg/L; was seriously inhibited when the daily addition was more than 50 mg/L; and was in normal operation when the ratio of the concentration of heavy metals daily added to that of activated sludge (dry matter) was less than 0.064% and the total concentration of dissolved, mixed heavy metals in the system was less than 1.0 mg/L. The results show that mixed heavy metals had a much stronger toxicity to an anaerobic system than each of the single heavy metals.

Key words: anaerobic digestion, heavy metal, inhibition.

Study on the Total Amount Control of Atmospheric SO_2 Emission in Handan City, Hebei Province. Fang Dong et al. (Institute of Nuclear Energy Technology, Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 14—18

The current status of SO_2 pollution in Handan City has been evaluated by using the general programme LEECM-2 which can generate a matrix of urban air pollution transmission functions and the shares of contribution. Then based on this, the total amount control of atmospheric SO_2 emission was studied. The results show that the programme LEECM-2 provides a convenient and practical calculation tool for the total amount control of air pollution, which will be helpful to promote the efforts for the total emission control in small-and medium-sized cities. The results also show that the basic reduction, equal weight reduction, source intensity optimization and economic optimization must be taken into an integrated account to develop a pollution reduction strategy for fairly and reasonably sharing the emission based on the principle of polluter pays.

Key words: air pollution, total emission control,

environmental management.

Experiment-based Evaluation of the Materials for Removal of Fluorides from Drinking Water. Qu Changling et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 19—22

The optimum conditions for polyaluminum species, CF-1 and PC85-3 to remove fluorides from drinking water, such as pH value, ageing and agitation, were compared in detail and activated alumina, bone carbon and UR-3700 chelate resin were tested for their equilibrium capacity of fluoride removal, the effect of water hardness, etc. The results show that polyaluminum species, CF-1 and PC85-3 removed the excessive fluorides from drinking water to an acceptable level for drinking use but had limited applications. Activated alumina and bone carbon were more effective filters for removing fluorides from drinking water. The optimum pH values for the fluoride removal by polyaluminum species were 6—7. The eficiency of fluoride removal was the same at water temperatures ranged from 10— 30 C. The stirring time of 1—3min and agitation time of 10—15 min were satisfatory for fluoride removal from drinking water. The equilibrium capacity of fluoride removal for activated alumina was 0. 89—1. 75mg/g. The eficiency of fluoride removal was related to pH, concentration of fluoride, salinity and hardness.

Key words: fluoride removal, polyaluminum, activated alumina, bone carbon, drinking water.

Selection of the Methods for Extraction and Determination of Extracellular Polymers from Anaerobic Sludge. Liu Zhijie et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 23—26

Extracellular polymers (ECPs) were extracted from 4 kinds of anaerobic sludge by using 6 different ECPs extracting processes, i. e., sulfuric acid process, sodium hydroxide process, ethylenediaminetetraacetic acid (EDTA) process, boiling benzene process, distilled water process and steaming process, which have been used to extract ECPs from activated sludge. The concentrations of polysaccharides in the extracts were determined by both the phenol-sulfuric acid method and the anthrone-sulfuric acid method, and the concentrations of nucleic acid were also measured to examine the degree of cells damaged. The results show that the sulfuric acid process can extract more ECPs from anaerobic sludges, with a less degree of damage to cells, than other processes. The phenol-sulfuric acid method was found more suitable to measure the concentration of polysaccharide. The level and composition of ECPs in anaerobic sludges were also discussed.

Key words: anaerobic sludge, extracellular polymer, extraction method, sulfuric acid process for ECP extraction.

Levels of Mercury in Soil and Their Geographical Distribution in Tibet. Zhang Xiaoping et al. (Changchun Institute of Geography, Chinese Academy of Sciences, Changchun 130021): *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 27—30

205 Samples of soil were taken from different sites in Tibet and analysed for their levels of mercury in soil. The data obtained were processed by using a method for mathematical programming statistics on a microcomputer and making some related computations. The results show that the average level of mercury in soils from Tibet was 0. 021 mg/kg and significantly lower than the average national level of 0. 04 mg/kg. The level of mercury in soil was distributed in Tibet with a total trend of gradually decreasing from the southeast to the northwest that was consistent with the direction of changes in the zonal successions of vegetation and soil in Tibet. The level of mercury was closely related to the basic attributes of soil and mercury tends to be concentrated upto the organic matter and glutinous grains of soil.

Key words: mercury, soil, Tibet.

Study on the Treatment of Dye-stuff Wastewater with an Anaerobic/Aerobic Process. Zhu Jianrong et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 31—34

The results were reported from a study on the treatment of dye-stuff wastewater by using an anaerobic/aerobic process, wherein the anaerobic stage was carried out in a UASB reactor and the aerobic stage was using a conventional activated sludge process. The results show that with a raw dye-stuff wastewater of 1150— 1300 mg COD/L and 500 fold colourity (a colour scale meant by the number of dilution times leading to a colour that seems to be the colour of tap water) under the condition of HRT 6— 10 h at the anaerobic stage, the COD removal was more than 60% and the colourity was reduced to 50—100 folds. If followed by an additional 6 h aeration treatment, the total COD removal was up to 85%— 90% and the colourity was further reduced to about 20 folds. The spectrometric analyses of influent and effluent revealed that the decolouration of dye-stuff wastewater mainly took place at the anaerobic stage and was achieved through bilogical degradation. It was concluded that the anaerobic/aerobic process was a cost-effective way to treat a dye-stuff wastewater and was of a great value of practical application.

Key words: dye-stuff wastewater, UASB reactor, activated sludge process, COD removal, decolouration.

Study on the Total Mercury and Methyl Mercury Contaminations in Fish from the Songhuajiang