聚硅酸硫酸铁混凝剂的性能研究*

高宝玉** 宋永会

(清华大学环境工程系, 北京 100084) (山东矿业学院化工系, 济南 250031)

岳钦艳

(山东大学环境工程系, 济南 250100)

摘要 以硅酸钠、硫酸和硫酸铁为原料制备聚硅酸硫酸铁混凝剂(简称 PFSS), 考察了 PFSS 在不同条件下水解产物表面的ζ电位变化情况, 研究了 Fe/SiO_2摩尔比和投加量对 PFSS 除浊效果的影响, 试验了PFSS 的最佳混凝 pH 范围与 Fe/SiO_2摩尔比之间的关系, 探讨了其混凝机理. 结果表明, Fe/SiO_2摩尔比对 PFSS 水解产物的ζ电位、PFSS 的混凝效果以及 PFSS 适宜的最佳 pH 值范围都有影响; 当 Fe/SiO_2摩尔比达1.5左右时, PFSS 的混凝除浊效果趋于最佳.

关键词 无机高分子混凝剂, 聚硅酸硫酸铁, 硅酸聚合, ζ电位, 除浊.

在水处理领域内, 高度聚合的硅酸与金属离子一起可产生良好的混凝效果[1]. 将金属盐引入到聚硅酸中所制得的混凝剂称为聚硅酸金属盐混凝剂. 由于这种混凝剂的平均分子量高达200000[2], 有可能在水处理中部分取代有机合成高分子絮凝剂以避免毒性问题. 通常, 铁离子和铝离子被用作偶联金属离子, 偶联金属离子与硅酸的摩尔比可随不同的使用要求加以调整. 笔者制备了以铁离子作为偶联金属离子的聚硅酸硫酸铁混凝剂(PFSS), 并研究了 PFSS 的性能等.

1 实验部分

1.1 主要仪器和试剂

JS94E 型微电泳仪, 722型光栅分光光度计, ZD-4型浊度计, J6-1A 搅拌器, pHS-2型酸度计. 模数(M)为3.21的硅酸钠(工业品), 高岭土(C.P.), 其它试剂均为 A.R.级.

1.2 PFSS 的制备

取一定量的硅酸钠用蒸馏水稀释到一定浓度, 用硫酸溶液调 pH 值, 放置一定时间使硅酸有一定的聚合度, 然后加入一定量的硫酸铁, 稍加热使硫酸铁溶解, 熟化2h 后可制得 PFSS 混凝剂(液体), 该混凝剂中 SiO_2的含量为2.0%, 具有不同的 Fe/SiO_2摩尔比.

1.3 混凝实验方法

用高岭土和蒸馏水配制试验水样. 于1L 蒸馏水中加入1g 高岭土, 加入0.032g Na_2CO_3使水样的碱度在0.8- 1.0meq/L 范围. 于500ml 水样中加入一定量的 PFSS, 以120 r/min 搅拌混合2min, 然后以60r/min 慢搅7min, 快速取约50ml 水样测ζ电位, 其余静置10min 后于液面下约2cm 处取上清液测浊度. 测定浊度时, 以蒸馏水作空白, 用"标准肼"浊度液校正. 实验过程中, 水样 pH 值用稀 HCl 或 NaOH 溶液进行调节.

1.4 ζ电位测定方法

用 JS94E 型微电泳仪进行测定(上海华东师范大学与上海市杰成实业有限公司合作研制)胶体颗粒表面的ζ电位, 该微电泳仪采用0.5cm 厚的玻璃杯电泳池, 电极内置在电泳池内, 样品用量极少, 每次仅0.5ml 左右. 正负换向时间为0.30s 至1.20s 连续可调, 采样时间仅需3- 10s, 电极间电压可根据需要调节(一般采样10mV). 采用温度采样探头自动连续对环境温度进行采样, 返回计算机自动调节参数, 用于计算ζ单位. 计算时, 采用计算机多媒体技术, 自动对经放大1500倍的微细颗粒(粒径范围为0.5- 10μm)连续"拍照", 提供双

* 煤炭高校优秀青年科学基金资助课题
** 工作单位: 山东大学环境工程系
收稿日期: 1996-10-29

向共4幅伪彩色图象进行分析计算.

2 实验结果与讨论

2.1 高岭土粒度分布情况

扫描电镜测得试剂高岭土的硅铝比为1.43,用粒度分布仪测得试剂高岭土粒度分布情况见表1.结果表明,试剂高岭土粒径主要分布在4-9μm范围内(约占62%),10μm以下的颗粒占75.70%,这与天然水中产生浊度的微粒的情况相当(天然水中产生浊度的微粒主要是粒径小于10μm的土壤颗粒[3]).

表1 试剂高岭土的粒度分布

粒 径/μm	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	9-10	>10
粒度分布/%	1.50	3.90	6.05	9.86	12.25	14.25	15.64	9.80	2.45	24.30

2.2 PFSS在不同pH值下的ζ电位值

PFSS样品稀释100倍,铁浓度在1.67×10^{-3}-3.34×10^{-3}mol/L范围(若铁浓度太高,则由于胶体颗粒太多,不便测定ζ电位值;但若铁浓度太低,则由于胶体颗粒太少,不利于ζ电位的准确测定),稀释液的pH值用稀HCl或NaOH溶液进行调节,然后测ζ电位值.由于PFSS水解沉淀物的表面会吸附一定数量溶解态的PFSS水解产物,因此,通过测定沉淀物的ζ电位便可大致说明PFSS水解产物的ζ电位变化情况.图1给出了Fe/SiO_2摩尔比分别为0.5和1.0的PFSS混凝剂的ζ电位值随pH变化情况,并与$Fe_2(SO_4)_3$溶液(铁浓度为3.34×10^{-3}mol/L)及聚硅酸(PSA)溶液(SiO_2浓度为3.33×10^{-4}mol/L)的情况进行了比较.结果表明,在PFSS中,由于聚硅酸与铁盐的共存,影响铁盐及聚硅酸的ζ电位值;在相同pH值情况小,PFSS的ζ电位值高于PSA的ζ电位值,低于$Fe_2(SO_4)_3$的ζ电位值;Fe/SiO_2摩尔比越小,PFSS的ζ电位值就越趋于PSA的ζ电位值;反之,PFSS的ζ电位值就越趋于$Fe_2(SO_4)_3$溶液的电位值.这种由于Fe/SiO_2摩尔比的不同而导致的PFSS的ζ电位值的不同,可能使具有不同Fe/SiO_2摩尔比的PFSS适应的最佳混凝pH值范围发生变化.

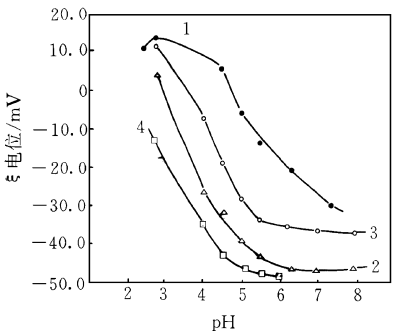

图1 PFSS的ζ电压随pH变化情况
1. $Fe_2(SO_4)_3$ 2. PFSS Fe/SiO_2=0.5
3. PFSS Fe/SiO_2=1.0 4. PSA

2.3 Fe/SiO_2摩尔比对PFSS混凝效果的影响

PFSS的投量以体积计,1L水样中加入0.25ml PFSS(PFSS中SiO_2含量固定为20g/L,铁含量按Fe/SiO_2摩尔比进行调整),水样的pH值为8.0左右,结果见图2.结果表明,Fe/SiO_2摩尔比对PFSS的混凝效果有明显影响,PFSS的混凝除浊效果随着Fe/SiO_2摩尔比的增大而提高,当Fe/SiO_2摩尔比达1.5左右时,PFSS的混凝效果趋于最佳.

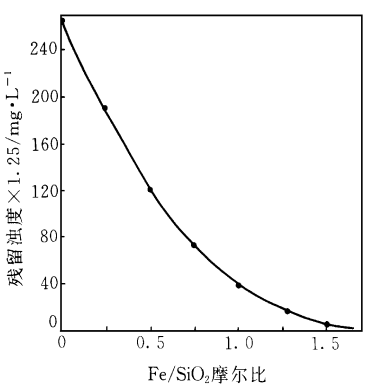

图2 Fe/SiO_2摩尔比对PFSS混凝效果的影响

2.4 PFSS的投加量对混凝效果的影响

以Fe/SiO_2摩尔比分别为0.5、1.0和1.5的PFSS样品进行试验,结果见图3.结果再次表明,Fe/SiO_2摩尔比越高,PFSS的混凝效果越好;对于Fe/SiO_2摩尔比为1.5的PFSS,当其投量为0.19ml/L时,除浊效果达最佳,过量投药不会引起高岭土悬浮液的再稳定;对于Fe/SiO_2摩尔比为1.0的PFSS,其投量达0.375ml/L时,才得到非常清澈的上清液,而

对于 Fe/SiO_2摩尔比为0.5的 PFSS, 则需更大的投药量才能达到较好的混凝效果.

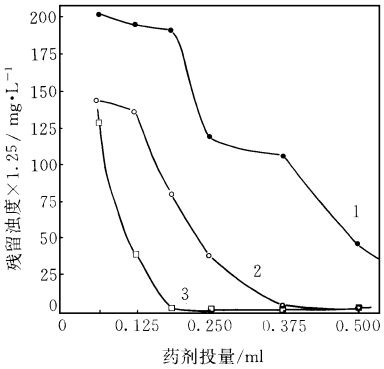

图3 PFSS 投药量对混凝效果的影响
1. Fe/SiO_2= 0.5 2. Fe/SiO_2= 1.0 3. Fe/SiO_2= 1.5

2.5 PFSS 适应的 pH 值及混凝机理探讨

药剂投量固定为1mg/L(以 SiO_2 计), 实验结果见图4. 结果表明, Fe/SiO_2 摩尔比对 PFSS 适宜的除浊 pH 值范围有一定的影响, 对于 Fe/SiO_2摩尔比小的 PFSS, 在较低的 pH 值范围内取得良好的除浊效果, 随着 Fe/SiO_2 摩尔比升高, PFSS 最佳除浊 pH 值范围稍向较高的 pH 值区域移动, 这种移动的幅度随着 Fe/SiO_2摩尔比的增高而加大. 利用 PFSS 的这一特性, 在实际应用中, 可根据不同的使用要求通过调整 Fe/SiO_2摩尔比来制备合适的 PFSS 混凝剂.

图4中 ζ 电位与 pH 值关系曲线表明, PFSS 用于混凝高岭土悬浮液时, 可在悬浮液

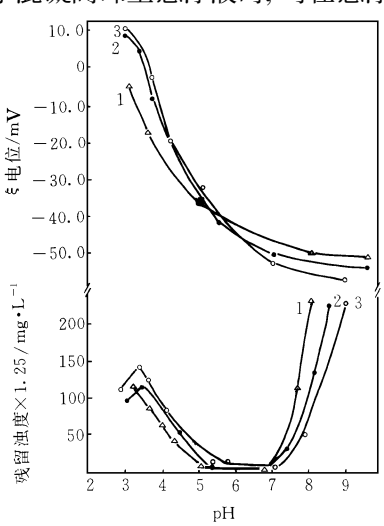

图4 不同 pH 下的 ζ电位及上清液残留浊度
1. Fe/SiO_2= 0.5 2. Fe/SiO_2= 1.0 3. Fe/SiO_2= 1.5

颗粒表面带有较大负电荷的情况下达到良好的除浊效果, 说明把电中和作用作为判断混凝剂混凝效果好坏的主要依据, 不能准确反映混凝过程中的实际情况, 应视混凝剂的种类和特性不同而具体分析.

探讨 PFSS 的混凝机理时, 应全面考虑: ①作为多聚物的聚硅酸的一般性质; ②铁盐的一般性质; ③聚硅酸中的硅羟基与铁离子及铁离子水解产物间的相互作用情况。当 PFSS 用作混凝剂投进要处理的水中后, 一方面: ①由于稀释作用和 pH 值的升高会引起铁盐水解程度的变化和形态的转化; ②铁水解产物与聚硅酸结合; ③由于 pH 值的升高导致聚硅酸的进一步聚合直至形成溶胶物; 另一方面: ①铁各水解产物则在混合过程中被水中悬浮物颗粒所吸附使颗粒脱稳; ②聚硅酸大分子或溶胶对吸附了铁水解产物的悬浮物质产生架桥及粘附作用而产生大的絮体, 从而取得净水效果. 以上过程同时进行, 且可迅速完成, 在 PFSS 最佳的除浊 pH 值范围内, 由于凝聚了的悬浮物带有较大的负电荷, 表明 PFSS 的混凝过程显然不同于传统的铁盐混凝剂, PFSS 表现出吸附架桥及粘附卷扫的典型特征.

3 结语

PFSS 是一种新型无机高分子混凝剂, 具有良好的混凝效果, Fe/SiO_2 摩尔比对 PFSS 的混凝效果、水解产物的 ζ电位、最佳除浊 pH 值范围等都有较大的影响. 由于这类混凝剂制备方法简便、无毒、混凝效果好, 且可根据处理对象的 pH 值不同, 通过改变 Fe/SiO_2摩尔比调整 PFSS 的配方来取得良好的混凝效果. 可以认为, 随着对该类混凝剂研究的不断深入, 该类药剂的推广应用价值将越来越被人们认识和接受.

参 考 文 献

1 Takao Hasegawa et al.. US 4, 923, 629, 1990
2 Takao Hasegawa et al.. Water Nagoya´89, ASPACIWSA. 1989, 31S-05-A8. 152
3 许保玖等. 当代给水与废水处理原理. 北京: 高等教育出版社, 1990: 165

A set of laboratory apparatus was established for recovery of styrene monomer from waste polystyrene. The influence of various reaction factors were investigated, such as temperature, pressure, amount of catalyst. On the laboratory condition, the yield of liquid product which contains 55.5% styrene monomer is 97.6%. The economic balance of this process was estimated when amplifying to industrial scale. It shows that higher profit can be attained and waste polystyrene plastics can be reclaimed. The pyrolysis mechanism was also discussed.

Key words: catalytic degradation, reclamation, styrene monomer, waste polystyrene plastics.

Study on The Property of Coagulant Polymeric Ferric Silicate-Sulfate (PFSS). Gao Baoyu (Dept. of Environ. Eng., Shandong University, Jinan 250100), Song Yonghui (Dept. of Chem. Eng., Shandong Institute of Mining and Technology, Jinan 250100): *Chin. J. Environ. Sci.*, **18**(2), 1997, pp. 46-48

Polymeric ferric silicate-sulfate (PFSS), a new kind of coagulant, has been prepared by using sodium silicate, sulfate acid and ferric sulfate as raw materials. The Zeta potential (ζ) of hydrolyzate of PFSS was measured at various pH values so as to know its electrokinitic natures. The effects of Fe/SiO_2 molar ratio and dosages on the coagulation were investigated. Also, the optimum pH range for coagulation was examined in respect to the molar ratio of Fe to SiO_2. Finally, the coagulation mechanism of PFSS for kaolinite suspension was discussed. The experimental results showed that the molar ratio of Fe/SiO_2 has effect on the Zeta potential (ζ) of hydrolyzate of PFSS, the turbidity removal result of PFSS for kaolinite suspension, and the pH range suitable for coagulation. The turbidity removal effect of PFSS for kaolinite suspension tends to reach optimum when the molar ratio of Fe/SiO_2 is or more than 1.5.

Key words: inorganic polymer coagulant, polymeric ferric silicate-sulfate, polymerization of silicic acid, turbidity removal.

Predication Teratogenicity of Chemicals Using Hydra Regeneration Assay. Cheng Qingyao et al. (Dept. of Biology, Anhui University, Hefei 230039), Ji yuantang et al. (Anhui Medical University, Hefei 230032): *Chin. J. Environ. Sci.*, **18**(2), 1997, pp. 49-51

In this paper, the hydra polyps regeneration assay was used to screen and predict the teratogenicity of sodium benzoate, sodium pyruvate, sodium fluride, sodium penicillin, and sodium nitrite. The results showed that sodium nitrite, sodium fluride and sodium benzoate are teratogens, while sodium penicillin and sodium pyruvate are not teratogens. These experimental results accord with the results of mammalian teratogenicity assay. The test is valuble to screen and predict teratogenicity of chemicals.

Key words: hydra, regeneration, teratogenicity.

Studies on Degradable Calcium Polyphosphate Fibers. Chang Qing (Dept. of Environ. Eng., Lanzhou Railway College, Lanzhou, 730070), Shi Zongli and Li Chongan (Dept. of Civil Eng., Lanzhou Railway College, Lanzhou 730070): *Chin. J. Environ. Sci.*, **18**(2), 1997, pp. 52-53

Calcium polyphosphate fibers have been prepared. The research showed that the structure of the fiber is glass state, the tensile strength is 1.90GPa, the modulus of elasticity is 67.5GPa, and the fibers are chemically degradable. So it can be used as reinforcing fibers for degradable composite materials.

Key words: calcium polyphosphate, degradation, fiber, composite material.

Determination of Trace Thiodicarb in Soil by Reversed-Phase High Performance Liquid Chromatography with Supersonic Extraction. Xu Guangtong and Li Dee (Dept. of Applied Chemistry, Shandong Institute of Building Materials, Jinan 250022): *Chin. J. Environ. Sci.*, **18**(2), 1997, pp. 54-57

In this paper, a method for determination of trace thiodicarb in soil by reversed-phase high performance liquid chromatography (RP-HPLC) with supersonic extraction where methanol was used as extraction solvent was presented. The supersonic extraction conditions for thiodicarb were selected. Analyses were performed on a 150×4.6mm octacedylsilica (ODS) bonded phase column in 14 minutes. Methanol/water (60/40) mobile phase was used. Ultraviolet detector was used for detection in 240 nm wave length. The linearity of the developed method was verified. The relative standard deviation (RSD) of the method was 1.48%. The average recovery rate was 100.7%. The quantitation limit was 0.01μg/g. The detection limit was 0.042ng. In addition, the degraded rule of thiodicarb in soil was studied.