

运河水中悬浮物和底泥上有机污染物的探查

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摘要 利用 GC/MS/DS 系统和保留指数, 对运河(常州段)悬浮物和底泥上的有机污染物进行了概要分析。结果显示, 该段河流的悬浮物和底泥上含有直链烷烃、多环芳烃、直链醛酮、烷基磺酸、苯酯类、邻苯二甲酸酯类、硝基联苯、二苯砷、醇类、羧酸类等有机污染物和致癌物。河流悬浮物和底泥上所鉴定出的有机污染物数量相当, 浓度范围基本一致。同一段面底泥上的浓度稍高于悬浮物上的浓度; 枯水期悬浮物上的浓度稍高于丰水期悬浮物上浓度。

关键词 有机污染物, 悬浮物, 底泥, 运河。

河水中的有机污染物在水相和颗粒物之间存在一个吸附和解吸的动态过程, 由于各有机污染物的物理化学性质相差甚大, 在两相间的分配差异也很大。吸附了有机污染物的颗粒物沉降于河底后, 将作为有机污染物长期的潜在的释放源, 对水生生物和人体健康产生危害。研究悬浮物和底泥上的有机污染物具有特殊重要的意义^[1-3]。

1 实验材料和方法

1.1 样品预处理

1.1.1 样品

底泥(A)采自运河(常州)丁埭段面; 悬浮物(B)采自运河(常州)丁埭段面(丰水期); 悬浮物(C)采自运河(常州)丁埭段面(枯水期); 悬浮物(D)采自运河(常州)五星段面。

现场所采河道中心表层底泥样, 用布氏漏斗抽滤, 压干, 取少量滤饼测含水量, 其余部分称重后加入约 5 倍含水量的无水硫酸钠, 拌匀并研磨至 80 目以下。悬浮物样用 60 L 水样, 静置过夜, 移去上层清水, 沉淀抽滤, 压干, 其余处理同底泥样。

1.1.2 提取和分离

取各悬浮物和底泥样品 20 g 左右(干重), 在索氏提取器中用二氯甲烷提取 8 h, 提取液经无水硫酸钠干燥后, 用 K-D 浓缩器浓缩至 5 ml 左右。将活化后的层析硅胶用正己烷湿法装柱,

硅胶层上加约 1 cm 高的无水硫酸钠层, 并用 20 ml 正己烷淋洗柱子。用 0.5 ml 层析硅胶充分吸附样品, 自然挥发至干, 装入柱上端。依次用正己烷; 正己烷/二氯甲烷($V/V=8/2$); 二氯甲烷; 二氯甲烷/甲醇($V/V=40/1$)和甲醇各 20 ml 洗脱, 将每份样品分成 5 组, 即 F1...F5 组。各洗脱液经干燥后用带 Snyder 柱的 K-D 浓缩器浓缩至 1 ml, 自然挥发至 0.2 ml, 备作分析。

1.2 分析鉴定

样品采用 Vista-6000 型气相色谱仪和 Finnigan MAT4510 型色谱-质谱仪进行分析测试, 充分利用数据系统的功能进行质谱图处理和检测, 同时制作和处理了大量的质量色谱图, 并配合以保留指数来进行定性分析。采用多重内标相对重量校正因子法进行定量分析^[4-5]。由于缺乏大量的标准参考化合物, 部分化合物系参考同系物或类似元素化合物的校正因子来进行定量计算。

2 结果与讨论

2.1 正己烷组(F1)

本组为非极性组分, 主要为直链烷烃。图 1 为悬浮物(D)的 F1 组重建离子色谱图和烷烃碎片 $m/e85$ 的质量色谱图, 可以看到 $C_{14}-C_{35}$ 的直链烷烃存在, 浓度 0.1—5.62 mg/kg(干重)。

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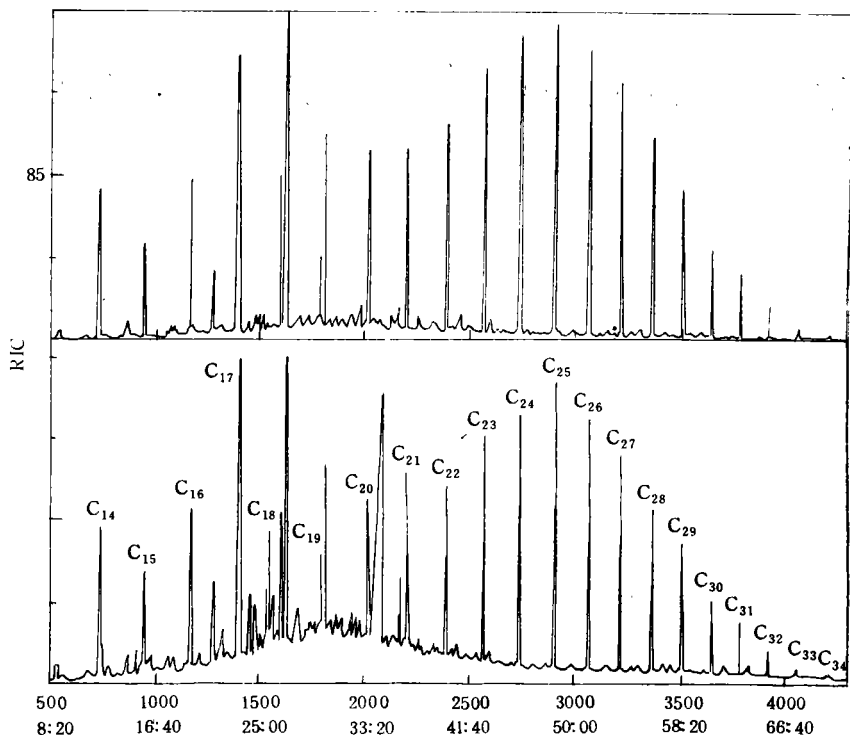


图1 悬浮物(D)F1组重建离子色谱图和烷烃特征离子质量色谱图

底泥(A)检出了 C_{12} — C_{30} 直链烷烃 19 种, 浓度 2.11—19.62 mg/kg(干重)。悬浮物(B)检出 C_{13} — C_{33} 直链烷烃 21 种, 浓度 0.10—4.74 mg/kg。悬浮物 C 检出 C_{14} — C_{31} 直链烷烃 18 种, 浓度 1.08—23.27 mg/kg(干重)。

2.2 正己烷/二氯甲烷组(F2)

F2 组鉴定出的化合物主要是多环芳烃, 图 2 为底泥(A)F2 组的色谱图, 显示其成分的复杂性。对于这类化合物的鉴定, 先通过 GC/MS/DS 系统获得各色谱峰的质谱图及各种异构体的特征离子质量色谱图, 再利用多环芳烃的保留指数系统进一步鉴定。具体步骤是用加入法确定几个计算保留指数的基准化合物, 将计算的结果与文献值^[6]比较, 结果见表 1。从二环至五环的多环芳烃母核及其烷基取代异构体在 F2 中均有检出; 六环芳烃也有少量检出。其中有许多强致癌性的多环芳烃。

2.3 二氯甲烷组(F3)

本组含有 3 类化合物, 第一类是醛和酮类, 多数是直链醛酮, 其中直链酮-[2]在底泥(A)中检出 4 种, 浓度 0.17—0.24 mg/kg(干重); 在

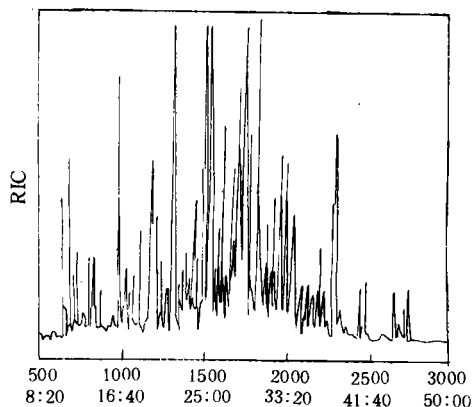


图2 底泥(A)F2组重建离子色谱图

悬浮物(B)中检出 5 种, 浓度均 <0.1 mg/kg(干重); 在悬浮物(C)中检出 6 种, 浓度均 <0.1 mg/kg(干重)。直链酮-[3]在底泥(A)中检出 4 种, 浓度 0.14—0.16 mg/kg(干重); 在悬浮物(B)中检出 3 种, 浓度均 <0.1 mg/kg(干重); 悬浮物(C)中检出 6 种, 浓度均 <0.1 mg/kg(干重)。直链醛在悬浮物(D)中检出 6 种, 浓度均 <0.1 mg/kg(干重)。第二类是烷基磺酸苯酯类化合物, 烷链为 C_{12} — C_{18} , 在底泥(A)中检出了

表 1 F2 组中主要有机污染物及含量

化 合 物		致癌 性 ^[7-8]	含 量 [mg/kg(干重)]			
名 称	分子式		底泥(A)	悬浮物(B)	悬浮物(C)	悬浮物(D)
联苯	C ₁₂ H ₁₀		0.25	0.10	0.15	<0.10
二苯醚	C ₁₂ H ₁₀ O		0.33		0.30	
萘烯	C ₁₂ H ₈	—	<0.10	0.10	0.10	
萘	C ₁₂ H ₁₀	—		0.30		<0.10
4-甲基联苯	C ₁₃ H ₁₂		0.10		0.18	<0.10
3-甲基联苯	C ₁₃ H ₁₂		0.10		0.30	<0.10
芴	C ₁₃ H ₁₀		0.79	0.50	0.98	0.40
4-甲基氧芴	C ₁₃ H ₁₀ O				0.19	0.10
甲基芴	C ₁₄ H ₁₂		0.52—0.75(3种)		0.67—0.77(2种)	均<0.10(5种)
菲	C ₁₄ H ₁₀	—	3.51	1.34	2.47	3.08
蒽	C ₁₄ H ₁₀	—	1.74	0.71	0.41	0.49
咔唑	C ₁₂ H ₉ N	—	0.29		1.02	
1-苯基萘	C ₁₆ H ₁₂		0.58		0.90	0.10
甲基菲(蒽)	C ₁₅ H ₁₂		0.36—3.24(7种)	0.30—0.91(5种)	0.51—1.68(6种)	0.10—0.72(5种)
2-苯基萘	C ₁₆ H ₁₂		1.43		1.81	0.70
C ₂ 取代菲(蒽)	C ₁₆ H ₁₄		0.74—2.84(8种)	0.10—0.64(10种)	0.39—0.85(6种)	0.10—0.24(6种)
萤蒽	C ₁₆ H ₁₀	—	4.48	1.11	4.27	4.53
芘	C ₁₆ H ₁₀	—	4.91	1.03	0.53	2.49
C ₃ 取代菲(蒽)	C ₁₇ H ₁₆		0.19—1.52(9种)	0.10—0.26(9种)	0.10—0.33(8种)	
苯并[a]芴	C ₁₇ H ₁₂	—	2.24	0.10	0.75	
苯并[b]芴	C ₁₇ H ₁₂		0.95	0.23		
苯并[ghi]萤蒽	C ₁₈ H ₁₀	—	<0.10		0.26	
苯并[c]菲	C ₁₈ H ₁₂	++	0.63	0.10	0.18	0.44
苯并[a]蒽	C ₁₈ H ₁₂	+	1.37	0.17	0.56	2.05
三亚苯	C ₁₈ H ₁₂		2.57	0.23	0.88	2.64
甲基苯并[a]蒽类	C ₁₉ H ₁₄	—/+	0.12—0.76(7种)	<0.10(3种)	<0.10—0.14(7种)	0.10—0.58(7种)
苯并[j]萤蒽	C ₂₀ H ₁₂	+++	0.71	0.10	0.11	1.92
苯并[b]萤蒽	C ₂₀ H ₁₂	+++	0.36	0.10	0.10	0.49
苯并[k]萤蒽	C ₂₀ H ₁₂	++	0.13	<0.10	0.40	1.45
苯并[e]芘	C ₂₀ H ₁₂	—/+	0.50	0.10	0.13	1.82
苯并[a]芘	C ₂₀ H ₁₂	++++	0.63	<0.10	0.23	1.47
苉	C ₂₀ H ₁₂	—	0.14	<0.10	0.11	0.40
苈	C ₂₀ H ₁₄	—	0.15	0.10	<0.10	0.20

34 种, 浓度 0.14—3.41 mg/kg(干重), 在悬浮物(B)中检出 35 种, 浓度 0.10—5.86 mg/kg(干重); 悬浮物(C)检出 43 种, 浓度 0.10—3.57 mg/kg(干重); 悬浮物(D)检出 9 种, 浓度 0.14—0.90 mg/kg(干重)。第三类化合物为邻苯二甲酸酯类, 主要是二丁酯和二辛酯, 在 4 份样品中均有检出, 浓度 1.16—4.38 mg/kg(干重)。在悬浮物(C)中还检出了硝基联苯、二苯砜等化合物。

2.4 二氯甲烷/甲醇组(F4)

图 3 是悬浮物(B)F4 组的重建离子色谱图。

该组含有极性组分, 主要是醇类化合物, 从 C₁₂—C₃₀ 的直链第一醇大多被检出, 其中底泥(A)检出了 13 种, 浓度 0.10—0.52 mg/kg(干重); 悬浮物(B)检出 13 种, 浓度 0.47—10.27 mg/kg(干重); 悬浮物(C)检出 8 种, 浓度 0.29—9.72 mg/kg(干重); 悬浮物(D)检出 11 种, 浓度 0.10—3.20 mg/kg(干重)。也有相当部分的侧链第二醇, 但难以确定其侧链和羟基的位置。

2.5 甲醇组(F5)

本组为强极性组分, 主要成分为羧酸类化合物, 从正十四酸至二十一酸均有检出, 浓度

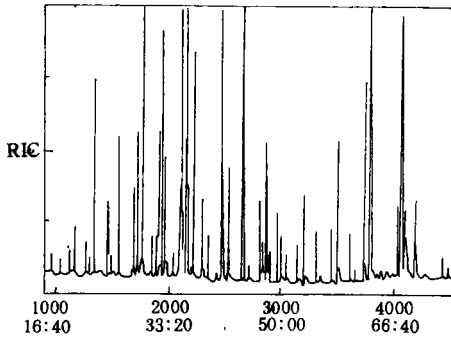


图3 悬浮物(B)F4组重建离子色谱图

范围 0.10—0.68 mg/kg(干重)。

3 结论

(1) 本文提出的预处理方法,直接加无水硫酸钠研磨干燥脱水,省去了风干步骤;采用

(上接第34页)

而农业的重复用水率变化不大,农业是直接完全用水的大户,新水用量占全市的61.5%,复用率仅为12%,仍存在着较大的节水潜力。今后应当努力提高农业的重复用水率,调整工农业用水比例,增加农产品的调入,以减少第一产业的新水用量。同时,继续提高第二产业的重复用水率,达到节约用水的目的,并为城市居民生活提供更多一些的生活用水。

(2) 从第二产业内部结构看,食品制造业的直接用水系数在全部行业中排第16位,而完全用水系数却排第3位,说明其用水的间接需求很大。这主要因为作为其原料行业的农业用水量较大的缘故。所以,应加强外地农产品的调入发展本市食品工业,加工生产,这样就等于间接调水入京,从而减少本市的用水压力。

(3) 仪器仪表及计量器具制造业、交通运输设备制造业、纺织业、机械工业、化学工业、电子及通信设备制造业、金属冶炼及压延加工业、炼焦煤气和煤制品业、是完全用新水系数较小的部门,今后应当大力发展,这亦符合北京市十年规划制定的方针。值得注意:炼焦煤气和煤制品业、化学工业的单位产值污水排放

硅胶层析预分离,简便实用,效果良好。

(2) 由GC/MS/DS系统并配合保留指数是鉴定复杂有机污染物的可靠方法之一。

(3) 本文的目的是对运河悬浮物和底泥上的有机污染物进行概要性探查。结果显示,该段河流悬浮物和底泥上含有相当数量的致癌物和有毒有机物,应引起足够的重视。

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量, COD产生量都很高,所以这两个行业在发展的同时更要注意加强技术革新,控制污染。

(4) 第三产业的重复用水率很低,其中一些部门用水量很大,如公用事业和居民服务业,行政机关,文教卫生科研事业等,其中存在着浪费的现象,这些部门的节水工作应当引起重视。应采取经济、法律、行政及技术等措施提高节水和回用水的比重(如利用中水设施),加强宣传,增强群众的节水观念,以达到节水目的。商业、饮食业、金融保险业的直接用水系数和完全用水系数较小,属于产值高,耗水少的部门,并且存在着很大的需求潜力,是今后应重点发展的行业。

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anionic surfactants in water and wastewater were determined at pH = 7.5 with azophloxine two-phase titration. The results of determination of anionic surfactants such as sulfates, sulfonates, benzenesulfonates, soap and phosphates etc, with azophloxine titration and methylene blue photometry, respectively, were compared and the interference tests and actual samples analysis were performed. All results show that the azophloxine titration was superior to the methylene blue photometry. The coefficient of variation was 1.0% ($n = 11$); minimum detectable concentration, 0.052 mg/L ($n = 21$); recovery of standard addition, 92.1%—110.2% on average 100.6% ($n = 14$). It was suggested that the concentration of anionic surfactants in water should be expressed in molar concentration or PSAA, instead of mg/L.

Key words: azophloxine, two-phase titration, anionic surfactants, wastewater.

Determination of Aniline in Polluted Water by Tridimensional Fluorescent Spectrometry. Wang Lun et al. (Dept. of Chemistry, Anhui Normal Univ., Wuhu 241000); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 63—64

The diagram of the tridimensional fluorescent spectrum (TDFS) of aniline was given by using an authors-developed program SIMS (surface image maker system) on a computer. The characteristic peak of aniline was defined. A new method for the determination of aniline by TDFS was suggested. When the concentration was in the range of 2.0×10^{-7} — 5.6×10^{-6} mol/L, a fine linear relationship between aniline concentration and relative fluorescence intensity was shown. The R. D. S. was 2.5%. The detection limit was 1.0×10^{-7} mol/L. With the method, aniline in polluted water from industry was determined satisfactorily.

Key words: aniline, fluorescence, polluted water.

Passive Integrating Measurement of Indoor and Outdoor Radon Concentrations. Zhai Pengji (Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100080); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 65—66

Both indoor and outdoor ^{222}Rn concentrations of an office building in Zhongguancun, Beijing, were determined by using a CR-39 detector and passive integrating radon monitor in different seasons of spring, summer, autumn and winter, with a total sampling time of 2—6 months. The

results show that the radon level found in the basement was higher than that in the office rooms above the basement and the indoor radon levels were higher than the outdoor radon levels. The error sources, including the effects of CR-39 random scanning and reading ways on the results of determination, were also discussed. It was found that, except in some individual cases, the extent of influence caused by different scanning ways was within the range of statistical variation.

Key words: radon, concentration, α tracks, CR-39 detector.

Total Radioactivity in Drinking Water for the Residents Living in Cities and Towns in Liaoning Province. Ma Junjie et al. (Liaoning Provincial Institute of Labour Hygiene, Shenyang 110005); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 67—68

The detection of total α and β radioactivities in the water samples collected from 50 waterworks companies and 40 self-supported water supply systems for factories or mines in the Liaoning Province was carried out in 1990 to 1994 and the results were reported. It was found that the total α radioactivity was in the ranges of 0.9×10^{-2} — 16.3×10^{-2} and 0.3×10^{-2} — 21.6×10^{-2} Bq \cdot L $^{-1}$, with the averages of 0.046 and 0.065 Bq \cdot L $^{-1}$ which were 8% and 15% over the national standards, respectively in the above two corresponding cases. The total β radioactivity was found in the range of 0.08—1.07 Bq \cdot L $^{-1}$, with less water samples which were exceeding the national standards. The results show that the natural radioactive nuclides were the major contributors to the total α radioactivity in the drinking water and the natural uranium compounds made the largest contribution by about 43% of the total α radioactivity.

Key words: uranium, α radioactivity, β radioactivity, drinking water, Liaoning Province.

Investigation on the Organic Pollutants in Suspended Solid Particles and Sediments in the Great Canal. Chen Jianlin et al. (Dept. of Environ. Sci. and Eng., Nanjing Univ., Nanjing 210093); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 69—72

A simple and effective pretreatment procedure was developed to generally analyze the organic pollutants in suspended solid particles and sediment in the Great Canal (Changzhou part) by using a GC/MS/DS system and a method of retention time index. The results show there were relatively high concentrations of carcinogens and

toxic organics in suspended solid and sediment. More attention should be paid to the fact.

Key words: organic pollutants, sediment, suspended solid.

HPLC Determination of Trace Phenols in Surface Water by Using a Concentration Technique Based on a Macromolecular Porous Resin GDX-502.

Bao Nan et al. (Center of Experiment, Shandong Univ., Jinan 250100); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 73–77

A simple method was described for the quantitative determination of phenols in surface water. The resin concentration technique was used instead of solvent extraction, by taking a macromolecular porous resin GDX-502 as an excellent adsorbent and dioxane as an excellent eluant. The eluate was analysed by a reversed-phase HPLC equipped with a UV detector. Recoveries of nine phenols were higher than 90%, except for 2, 4-dinitrophenol, and the average relative standard deviation ($n=5$) was 2.4%. The detection limits of nine phenols were 2.0–8.6 ng. Trace concentration at $\mu\text{g/L}$ level of these phenols pollutants can be determined. The developed method has been applied to determining phenols of urban lake water and river water with satisfactory results.

Key words: phenols, GDX resin, concentration, analysis by HPLC.

Study on the Economic Legal System for China's Sustainable Development.

Wang Mingyuan et al. (Center of Environmental Science, Peking University, Beijing 1000871); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 78–82

Economic instruments were pointed out to have a very important role to play in the process towards sustainable development in China, and in essence, to allow the environmental resources to be used on a charged basis and the principle of polluter pays to be actually performed. The economic instruments for use in the sustainable development should mainly include an environmental fees imposing system, an environmental taxation system, financial incentives systems, emission permits trade systems, assurance systems on obligation to environmental damage, and the like. A detailed discussion was made on the concepts, natures, roles, current statuses, perfections and implementations of both environmental fees imposition and taxation systems, and the relationship between both. The issues of the application of financial subsidization and emission permits trade systems to the sustainable development

in China were also analyzed. Finally, it was stressed that the related environmental legislations should be further perfected so as to make strengthened economic instruments and compulsory environmental management.

Key words: sustainable development, economic instrument, environmental fees, environmental taxation.

Study on the Ecological and Environmental Effects of Constructing a Long Oil Pipe Work.

Mu Congru and Yang linsheng (Institute of Geography, Chinese Academy of Sciences, Beijing 100101); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 83–87

The effects of constructing a long oil pipe work on the ecological and environmental elements, such as natural vegetation, forest, grasslands, farmlands, oasis, soils and wild animal habitats, were analyzed. The models for calculating the losses of 7 ecotypes caused by such a pipe work construction were developed. In studying the response strategies for environmental protection, 3 indicators representing the ability of ecological restorage were suggested to describe the extent to which a damaged surface ecosystem can be rehabilitated after the completion of such a work. Based on this, the measures were suggested to minimize the losses by such a pipe work and to speed up the rehabilitation of a damaged ecosystem.

Key words: long oil pipe work, environmental impact, damaged ecosystem, ecological rehabilitation.

Theoretical Analysis of an Internal Circulating Bio-Fluidised Bed Reactor.

Zhou Ping, Qian Yi (Dept. of Environ. Eng., Tsinghua Univ., Beijing 100084); *Chin. J. Environ. Sci.*, **16**(2), 1995, pp. 88–90

An analysis on the flow pattern, the organic matter degradation by biofilm, and the biofilm forming in an internal circulating three-phase biofluidised bed was conducted, based on the reactor theory, biofilm kinetics and hydrodynamics. It was found that D/ud was constant in the reactor and the efficiency factor was calculated for a general municipal wastewater treatment system and the relationship between circulating velocity and reactor size was established. Some possible optimization ways to increase the reactor efficiency was also suggested.

Key words: internal circulating three-phase biofluidized bed, reactor, kinetics, hydrodynamics.