

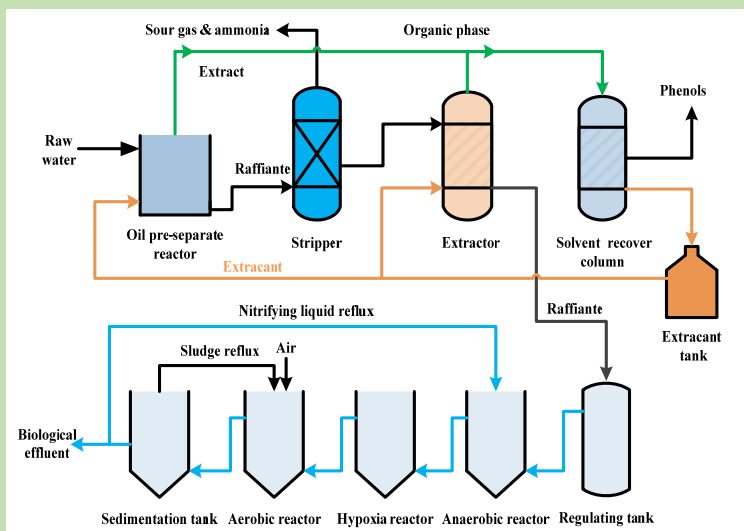
## Co-extraction and synergistic detoxification technology and its application in high-concentration wastewater from coal chemical industry

Hongbin CAO<sup>1\*</sup>, Gaojie XU<sup>1,2</sup>, Pengge NING<sup>1</sup>, Shaoyuan SHI<sup>1,2</sup>

1. Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

2. Zhengzhou Institute of Emerging Industrial Technology, Zhengzhou, Henan 450000, China

**Abstract:** High-concentration wastewater from coal chemical industry has attracted widespread attention because of complex composition, high concentration of pollutants, high toxicity and low biodegradability. It not only contains ammonia nitrogen, phenols and oil compounds with high concentration, but also contains highly toxic pollutants such as heterocyclic compounds and polycyclic aromatic hydrocarbons (PAHs). High-efficiency dephenolization and deep detoxification are the two major bottlenecks in wastewater treatment. In this work, the phenolic-oil co-extraction synergistic



detoxification technology was proposed from the perspective of process pollution control, and the special extractant IPE-PO was used to treat the high-concentration wastewater from coal chemical industry in Yunnan. The organic matter in the wastewater before and after treatment was detected by GC-MS, and compared with methyl isobutyl ketone (MIBK) extraction system which was used in industrially widely. After treatment using IPE-PO extractant, the average removal rates of chemical oxygen demand (COD), total phenol, ammonia nitrogen ( $\text{NH}_4^+-\text{N}$ ) and absorbance of organic matters at 254 nm ( $\text{UV}_{254}$ ) were 77.69%, 90.45%, 97.10% and 82.19%, respectively. Most of the toxic pollutants were removed, and the biodegradability of the wastewater was improved significantly. There were 101 kinds of organic matters in the raw water, after IPE-PO process, the types of organic compounds were reduced to 74 kinds. The process showed ascendancy in the treatment of toxic matters. After biochemical and advanced treatment, the COD of wastewater reduced from 31000~37000 mg/L to less than 100 mg/L, and the  $\text{UV}_{254}$  of wastewater reduced from  $197\text{ cm}^{-1}$  to  $0.5\text{ cm}^{-1}$ , which meet the wastewater discharge standard of China. Compared with the MIBK extraction system, the deep detoxification ability of the technology was proved. The operating cost does not exceed 10 yuan/t wastewater. The phenol-oil synergistic co-extraction detoxification technology with IPE-PO extractant is a feasible and efficient pretreatment method for coal chemical wastewater treatment.

**Key words:** coal chemical industry; high-concentration wastewater; phenol; synergistic detoxification; extraction technology

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作者简介: 曹宏斌(1971-), 男, 江苏省南通市人, 博士, 研究员, 环境化工专业, Tel: 010-82544845, E-mail: hbcao@ipe.ac.cn.

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# 酚油共萃协同解毒技术及其在煤化工高浓废水中的应用

曹宏斌<sup>1\*</sup>, 许高洁<sup>1,2</sup>, 宁朋歌<sup>1</sup>, 石绍渊<sup>1,2</sup>

1. 中国科学院绿色过程与工程重点实验室, 中国科学院过程工程研究所, 北京 100190

2. 郑州中科新兴产业技术研究院, 河南 郑州 450000

**摘 要:** 煤化工高浓废水因成分复杂、污染物浓度高、毒性大、可生化性低等特点受到环保行业广泛关注, 废水中含有高浓度的氨氮、酚类和油类物质及杂环化合物和多环芳烃等高毒性污染物, 高效脱酚和深度解毒是该类废水处理的两大瓶颈。本工作从过程污染控制角度提出了酚油共萃协同解毒技术, 配合研发的酚油联合脱除专用萃取剂 IPE-PO, 有针对性地处理云南某企业的煤化工高浓废水。用 GC-MS 检测了处理前后废水中的有机物种类, 并与工业应用广泛的甲基异丁基酮萃取剂(MIBK)萃取体系进行对比。预处理后废水中的化学需氧量(COD)、总酚、氨氮( $\text{NH}_4^+-\text{N}$ )、有机物的吸光度( $\text{UV}_{254}$ )平均脱除率分别为 77.69%, 90.45%, 97.10%和 82.19%, 去除了大部分有毒污染物, 废水的可生化性显著提高。处理后废水中的有机物种类从原水中的 101 种减至 74 种, 展现了该技术在处理有毒物质方面的优势。经生化处理和深度处理, 废水 COD 从 31000~37000 mg/L 降至 100 mg/L 以下,  $\text{UV}_{254}$  从 197  $\text{cm}^{-1}$  降至 0.5  $\text{cm}^{-1}$ , 可直接排入污水厂, 运行成本不超过 10 元/t。IPE-PO 萃取剂酚油协同共萃解毒技术在煤化工废水处理上是一种可行且高效的预处理方法。

**关键词:** 煤化工; 高浓废水; 酚油共萃; 协同解毒; 萃取技术

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## 1 前言

我国能源结构具有“富煤、贫油、少气”的特点, 煤炭是我国的基础能源和重要原料, 在一次能源结构中 将长期处于战略主体地位<sup>[1]</sup>。随着煤化工行业发展由快趋稳, 存在的问题不断暴露, 其中最受关注的是煤化工项目中的环保问题, 产生的大量污染物增加了项目的技术难度和经济成本, 危害人体健康。煤化工废水由于排放量大、污染物含量高、污染成分复杂、易产生难处置固体废物且引发二次污染等特点, 成为制约煤化工发展最重要的环境问题<sup>[2-7]</sup>。煤化工废水主要源于煤制气、煤制油和干馏等过程, 其组成和产生强度受煤种及转化工艺影响, 尤其是碎煤加压气化、煤直接液化和低温干馏等的废水, 浓度高、成分复杂、毒性强、水质波动大, 难以有效处理<sup>[8]</sup>。经过多年发展, 煤化工废水处理已形成酚氨回收-生化处理达标排放路线。酚氨回收方面, 德国鲁奇公司在 20 世纪率先开发了二异丙醚萃取剂(DIPE)和萃取-脱酸-脱氨工艺, 并应用于南非萨索和美国大平原煤制气项目。华南理工大学在国内率先使用甲基异丁基酮萃取剂(MIBK)开发出脱氨-萃取新工艺, 提高了多元酚的回收率, 废水中污染负荷指标仅为鲁奇工艺的 20%~60%<sup>[9-11]</sup>。但两种萃取剂的溶解度均较高, 二异丙醚为 0.94 g/100 g 水, 甲基异丁基酮达 1.7 g/100 g 水, 萃取后需将富酚有机相精馏再生萃取剂, 还需精馏萃取塔出水以回收溶解损失的萃取剂, 减少二次污染, 因此势必造成巨大能耗, 增加运行成本。煤化工废水尤其是煤中低温干馏废水(兰炭废水)中除酚类物质外, 还

含大量的强毒性杂环类物质、微细乳化油和纳米级焦粉/焦油, 对酚氨回收装置的正常运行带来巨大挑战, 这些强毒性物质进入生化段后可大量致死微生物, 导致生化处理设施瘫痪<sup>[12-15]</sup>。

本工作针对这一技术难题, 提出了针对高浓度酚氨废水的酚油联合脱除协同解毒技术。包括对废水成分进行详细解析, 并根据污染物解析结果设计了酚油联合脱除专用萃取剂 IPE-PO 和配合该萃取剂的强化解毒工艺, 将本工艺实验结果与工业应用广泛的 MIBK 流程结果进行了对比。

## 2 实验

### 2.1 实验试剂

废水(云南某煤气化厂), 浓硫酸(分析纯, 纯度 98%, 北京化工厂), 磷酸二氢钾、重铬酸钾、氢氧化钠、氯化铵和无水硫酸钠(分析纯, 北京化工厂), 福林酚、碳酸钠、4-甲基-2-戊酮和四氯化碳(国药集团化学试剂有限公司), 二氯甲烷(优级纯, 天津市光复科技发展有限公司), 高纯水(实验室自制)。

### 2.2 实验装置

UV9100A 型紫外-可见分光光度计(北京莱伯泰科仪器股份有限公司), 5B-3B(V8)COD 型消解仪(兰州连华环保科技有限公司), SHZ-88A 型水浴振荡器(苏州培英实验设备有限公司), OIL500 型红外测油仪(天津天光光学仪器有限公司), FE28 pH 计、FE38 电导率仪和 ME104 分析天平(上海梅特勒-托利多仪器公司), Milli-Q 型超纯水制备系统(美国 Millipore 公司), TOC-V

CPH 总有机碳分析仪(TOC, 日本岛津公司), RE52AA 旋蒸仪(上海亚荣生化仪器厂), DHG-9070A 电热恒温鼓风干燥箱(上海一恒科技有限公司), Agilent GC7890A-MS5975C 气相色谱-质谱联用仪(GC-MS, 美国安捷伦科技有限公司)。

2.3 水质指标分析方法

2.3.1 普通水质指标分析方法

主要水质指标及测定方法：重铬酸钾法测定化学需氧量(COD), 氨气敏电极法测定氨氮, 福林酚法测定总酚, 紫外分光光度法测定吸收 254 nm 波长紫外光的物质(UV<sub>254</sub>), 红外测量法测定油含量, 总有机碳分析仪测定总有机碳(TOC)和总无机碳(IC), 重量法测定悬浮物(SS)。

2.3.2 水相中有机物分析

按文献<sup>[16]</sup>方法, 将水样通过 0.45 μm 水系滤膜, 置于分液漏斗中, 用二氯甲烷分别在 pH=7, 12 和 2 的条件下萃取, 各萃取 3 次, 每次萃取剂用量 20 mL。合并萃

取液, 将其过无水 NaSO<sub>4</sub> 除水, 合并有机相。将干燥后的有机溶剂转移至茄型瓶中, 在 35℃ 的旋转蒸发仪中蒸发浓缩至 3~5 mL, 用氮气吹扫至 1 mL。溶液转移时均用二氯甲烷润洗 3 次, 以减少目标物质的损失。

GC-MS 测试条件, GC: 进样口温度 250℃, HP-5MS 毛细管色谱柱(325℃, 30 m×250 μm×0.25 μm), 柱箱程序升温 30℃ 保持 1 min, 5℃/min 升温至 120℃ 保持 3 min, 再以 5℃/min 速率升温至 270℃, 传输线温度 200℃; MS: 离子源温度 230℃, 扫描范围 50~500 aum, 进样量 1 μL, 分流比 99:1。

3 结果与讨论

3.1 废水水质分析

废水样品水质随时间等因素变化, 水质指标取连续 30 d 的数据统计, 如表 1 所示。废水中有机物的总离子流如图 1 所示。分析归纳了匹配度超过 60 的有机物。

表 1 煤气化废水水质特征

Table 1 Characters of coal gasification wastewater

pH	COD/(mg/L)	Total phenol/(mg/L)	NH <sub>4</sub> <sup>+</sup> -N/(mg/L)	UV <sub>254</sub> /cm <sup>-1</sup>
9.33~9.82	31300~37170	9930~12843	10036~14001	170~212.8
Oil/(mg/L)	Salt/(mg/L)	TOC/(mg/L)	IC/(mg/L)	SS/(mg/L)
3570~4615	18110~19120	11500	4211	762~1200

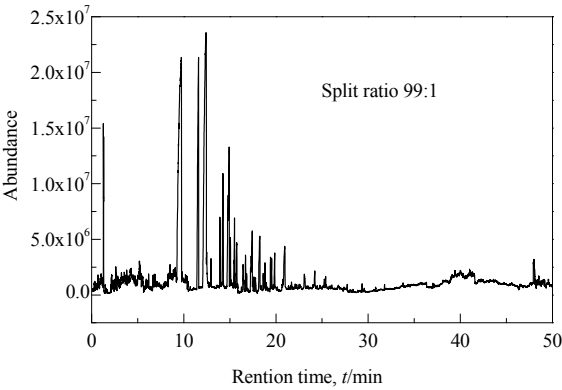


图 1 原水 GC-MS 总离子流图

Fig.1 The total ion chromatogram of raw water by GC-MS

从表 1 可以看出, 废水中污染物浓度高、毒性强, 具有高 COD、高酚值、高氨氮、高悬浮物、高含油量、高盐度、高 pH 等特点。废水毒性强是因为所含有机污染物成分复杂, 种类繁多。用 GC-MS 共检测出 101 种有机物, 其中酚类化合物有 52 种, 是废水中有机污染物的主要组成部分, 以单元酚、烷基取代酚、二元酚和烷氧基取代酚为主, 总酚浓度为 9930~12843 mg/L。还含少量吡啶、呋喃、喹啉、硫酚、酸酯、酮醚、哌啶、噻、胺、茛醇、醌、苯系物、多环芳烃、恶唑、咪唑和

吡唑等 49 种有机物, 该类废水生化需氧量与化学需氧量的比值(BOD/COD)仅为 0.12, 表明其毒性强、可生化性差、处理难度大。

3.2 预除油-蒸氨/酚油共萃协同解毒技术

针对该类废水的特点, 提出预除油-蒸氨/酚油共萃协同解毒技术, 其核心是采用富酚有机相进行预除油及酚油共萃。采用计算机辅助分子设计-实验验证方法, 基于中国化学品名录, 设计萃取效果好、解毒能力强的环境友好萃取剂 IPE-PO。该萃取剂为物理萃取剂, 根据相似相容原理, 萃取废水中的有机物, 对苯酚的萃取率为 100%, 对总酚的萃取率也有显著提高, 解毒性强, 与传统萃取剂二异丙醚(DIPE)和甲基异丁基酮(MIBK)的比较如表 2<sup>[17,18]</sup>所示。

根据 IPE-PO 和 MIBK 两种萃取剂的特点设计了两种萃取流程, MIBK 萃取剂溶解度大, 萃取后需蒸馏萃余液以回收溶解的萃取剂, 设计的萃取流程与工业上相似, 即蒸氨-萃取(二级)-蒸馏萃余液, 简称 MIBK 流程; 而 IPE-PO 的溶解度非常小, 仅为 MIBK 的 1/35, 无需蒸馏萃余液, 按预除油-蒸氨-萃取(二级)步骤设计实验, 简称 IPE-PO 流程。表 3 为 IPE-PO 和 MIBK 流程运行 25 个批次的统计结果, 各指标的平均值如图 2 所示。以

原水各指标为参照，各工段各污染物的脱除率见图 3。

表 2 三种萃取剂的性能比较<sup>[17,18]</sup>  
Table 2 Comparison of the property of three extractants<sup>[17,18]</sup>

Property	DIPE	MIBK	IPE-PO
Relative density (20 ℃/4 ℃)	0.724	0.80	0.79~0.83
Viscosity (25 ℃)/(mPa·s)	0.329	0.542	0.7~0.9
Boiling point (101.3kPa)/℃	68.3	115.9	120~180
Solubility in water (20 ℃)/%	0.94	1.7	0.048
Solubility of water in solvent/%	0.55	1.9	0.021
Distribution coefficient	20~30	60~70	60~70
Extraction rate of volatile phenol/%	99.6	99	100
Total phenol extraction rate of total phenol/%	60	80	90
Chemical stability	Stable	Stable	Stable
Azeotropic temperature with water/℃	61.4	87.9	98.9
Azeotrope component/%	96.4	75.7	7.1
Toxicity (rat oral)/(mg/kg)	8 470	Toxic/highly irritating	5000
Extractant price/yuan	22000	15000	13000~16000
Extractant application	Henan Yima Coal Gasification, Harbin Coal Gasification Plant	Harbin Coal Gasification Plant	Shanxi Qianyuan Energy Chemical Co., Ltd.

表 3 不同流程各工段出水水质(25 个批次数据)  
Table 3 The water quality of each stage of different processes (25 batches of data)

Process	Stage	pH	COD/(mg/L)	Total phenol/(mg/L)	NH <sub>4</sub> <sup>+</sup> -N/(mg/L)	UV <sub>254</sub> /cm <sup>-1</sup>
Raw water	—	9.33~9.82	31300~37170	9930~12843	10036~14001	170~213
IPE-PO process	Oil pre-separate	9.42~9.97	11890~15500	2882~4554	10036~13747	89~112
	Ammonia distillation	7.02~7.76	7675~12555	2354~2898	229~472	45~73
	First stage extraction	6.95~7.79	7150~9330	1201~1671	229~472	33~55
	Second stage extraction	6.67~7.71	6245~8580	848~1280	229~472	32~48
MIBK process	Ammonia distillation	6.98~7.68	11590~14370	4175~5128	256~489	61~90
	First stage extraction	7.37~7.9	43940~49510	933.8~1599	266~419	43~55
	Second stage extraction	7.57~7.9	45450~52370	789~1073	246~403	38~53
	Distillation	5.75~6.55	4741~6470	799~1016	187~387	27~41

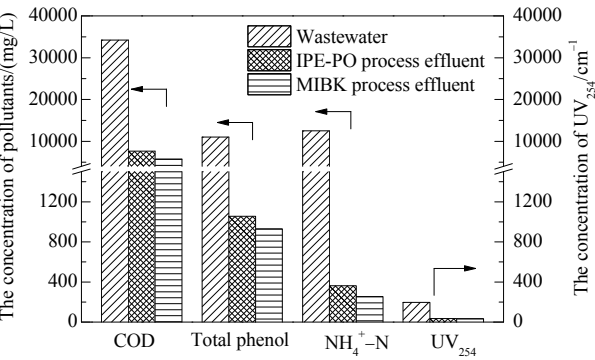


图 2 IPE-PO 流程和 MIBK 流程处理效果对比  
Fig.2 Comparison of pollutant removal effects between IPE-PO process and MIBK process

由表 3、图 2 和图 3 可知，废水经 IPE-PO 流程处理后，出水 COD 浓度为 6245~8580 mg/L，平均 COD 浓度为 7637 mg/L，COD 的平均去除率为 77.69%；出水总酚浓度为 848~1280 mg/L，平均总酚浓度为 1055 mg/L，总酚的平均去除率为 90.45%；出水氨氮浓度为 229~472 mg/L，平均氨氮浓度为 363 mg/L，氨氮平均去除率为 97.10%；出水 UV<sub>254</sub> 为 32~48 cm<sup>-1</sup>，平均 UV<sub>254</sub>

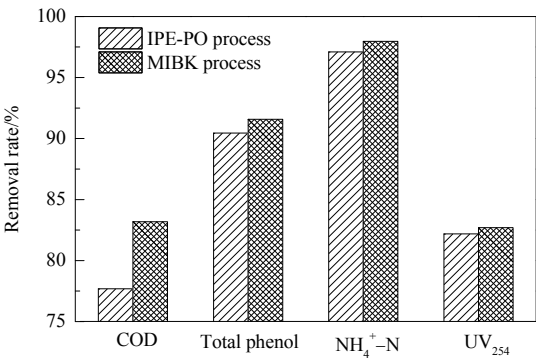


图 3 IPE-PO 流程和 MIBK 流程污染物去除率对比  
Fig.3 Comparison of pollutant removal rates between IPE-PO process and MIBK process

为 35 cm<sup>-1</sup>，UV<sub>254</sub> 的平均去除率为 82.19%。废水经过 MIBK 流程处理后，出水 COD 浓度为 4741~6470 mg/L，平均 COD 浓度为 5754 mg/L，COD 平均去除率为 83.19%；出水总酚浓度为 799~1016 mg/L，平均总酚浓度为 929 mg/L，总酚平均去除率为 91.58%；出水氨氮浓度为 187~387 mg/L，平均氨氮浓度为 254 mg/L，氨氮平均去除率为 97.97%；出水 UV<sub>254</sub> 为 27~41 cm<sup>-1</sup>，平

均  $UV_{254}$  为  $34\text{ cm}^{-1}$ ,  $UV_{254}$  平均去除率为 82.70 %。

由结果可见, MIBK 流程对 COD 的去除效果明显优于 IPE-PO, 出水平均 COD 浓度相差  $1883\text{ mg/L}$ , 而总酚、氨氮、 $UV_{254}$  的去除效果优势不明显, 分别相差  $126\text{ mg/L}$ ,  $109\text{ mg/L}$  和  $1\text{ cm}^{-1}$ , 表明 IPE-PO 流程萃取脱酚的能力与 MIBK 相当。IPE-PO 流程先对废水进行预除油, 降低废水的 COD 和总酚含量, 脱酸脱氨过程回收的氨水中有有机物浓度较低, 所得氨水品质较高。IPE-PO 萃取剂在水中溶解度小, 不需回收, 减少了回收萃取液中萃取剂的成本。与 IPE-PO 流程相比, MIBK 直接脱酸脱氨, 回收的氨水中有有机物浓度较高、品质较低, 需进一步处理, 且 MIBK 在水中溶解度较大, 需回收, 增加了处理成本。

对两个流程获得的萃取液进行分析, 并与废水对比, 结果如图 4(a)和 4(b)所示。由图可知, 废水经 MIBK

流程和 IPE-PO 流程处理后, 出水中污染物都很少, 表明这两种处理方式都能够很好去除废水中的污染物, 其中 IPE-PO 流程出水 GC-MS 图中的峰对应萃取剂的主要成分。由于 MIBK 流程和 IPE-PO 流程出水污染物浓度较低, 与原水分析分流比(99:1)相同时只检测出很少的有机物, 其中 MIBK 流程检出 8 种有机物, IPE-PO 检出 18 种, 部分污染物可能因仪器检出限而无法检测到, 不能全面了解出水的污染物。为进一步分析两个流程出水的污染物情况, 将进样分流比改为 4:1, 结果分别见图 4(c)和 4(d)。从图可看出, MIBK 流程出水中污染物多而杂, 但浓度较低, 而 IPE-PO 流程出水中污染物种类明显减少, 但保留时间为 5~10 min 的峰经质谱分析为 IPE-PO 萃取剂的主要成分。因未蒸馏萃取液, 少量萃取剂溶解残留其中, 这也是导致 IPE-PO 流程出水 COD 较高的原因。

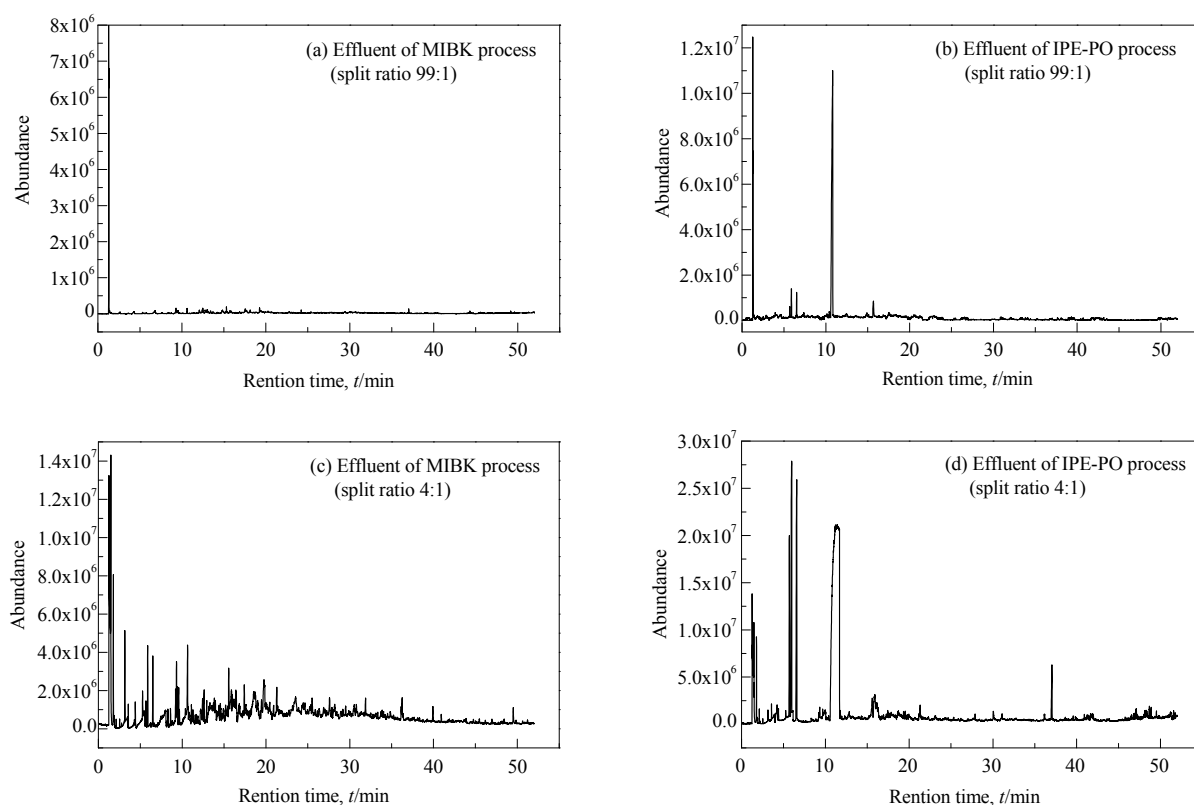


图4 GC-MS 总离子流图

Fig.4 GC-MS total ion chromatogram

结合 GC-MS 结果, 对废水及其分别经 IPE-PO 和 MIBK 流程预处理后的萃取液污染物种类进行比较, 结果列于表 4。原水按分流比 99:1 分析, MIBK 出水和 IPE-PO 出水按分流比 4:1 分析。由表可知, 废水原水中检测出匹配度大于 60 的污染物有 101 种, 经 IPE-PO 流

程处理后污染物减至 74 种, MIBK 流程处理后污染物为 106 种, 推测增加的物质为处理过程中(如蒸馏)产生的新物质, 或原水中污染物浓度较高, 掩盖了低含量的有机物, 当监测预处理出水时因分流比较小, 原水未被测出的低浓度污染物被检测到。

表 4 GC-MS 测定的煤气化废水预处理前后的有机物

Table 4 Organic matters before and after pretreatment of coal gasification wastewater by GC-MS

Classification	Organic compound	Raw water (101 species)	IPE-PO process effluent (74 species)	MIBK process effluent (106 species)
Phenolic compounds		52 species	12 species	17 species
	Phenol	+	—	+
	2-Methylphenol	+	—	+
	3-Methylphenol	+	—	+
	4-Methylphenol	+	—	+
	2-Methoxyphenol	+	—	—
	3-Methoxyphenol	—	—	+
	4-Ethoxyphenol	—	—	+
	3-Aminophenol	—	+	+
	4-Aminophenol	—	+	+
	2-Aminophenol	—	+	+
	4-Hydroxy-3-methoxy-benzenepropanol	—	—	+
	4,4'-Methylenebis(2,6-dimethylphenol)	—	—	+
	2,4-Dinitro-1-naphthol	—	—	+
	2-Methyl-6-t-octylphenol	—	—	+
	2-Methoxy-4-vinylphenol	—	—	+
	2,5-Di-tert-butylphenol	—	—	+
	4-Methyl-1-naphthol	—	—	+
	2,6-Dimethylphenol	+	—	—
	2-Ethylphenol	+	—	—
	3,5-Dimethylphenol	+	—	—
	2,4-Dimethylpheno	+	+	—
	2,3-Dimethylphenol	+	—	—
	4-Ethylphenol	+	—	—
	3-Methyl-5-ethylphenol	+	—	—
	2-Methoxy-4-methylphenol	+	—	—
	2-Methoxy-5-methylphenol	+	—	—
	3,4-Dimethylphenol	+	—	—
	Catechol	+	+	—
	2-Propylphenol	+	—	—
	2-Allylphenol	—	+	—
	2-Ethyl-5-methylphenol	+	—	—
	3,4,5-Trimethylphenol	+	—	—
	4-Ethyl-3-methylphenol	+	—	—
	2-Ethyl-4-methylphenol	+	—	—
	4-(2-Propenyl)phenol	+	—	—
	4-Propylphenol	+	—	—
	2-Ethyl-6-methylphenol	+	—	—
	3-Methylcatechol	+	—	—
	2,4,5-Trimethylphenol	+	—	—
	2,3,5-Trimethylphenol	+	—	—
	2,4,6-Trimethylphenol	+	—	—
	4-Methylcatechol	+	+	—
	2,5-Diethylphenol	+	—	—
	3-Methoxy-5-methylphenol	+	—	—
	2-Methyl-6-propylphenol	+	—	—
	Resorcinol	—	+	—
	2-Methylresorcinol	+	—	—
	5-Methylresorcinol	—	+	—
	2,5-Dimethylresorcinol	+	+	—
	2-Octadecylhydroquinone	—	+	—
	4,5-Dimethylresorcinol	+	—	—
	2,6-Dimethyl-1,4-benzenediol	+	—	—
	2-Methoxy-4-methylphenol	+	—	—
	4-Ethylresorcinol	+	—	—
	3-Acetylphenol	+	—	—
	2,3-Dimethyl-1,4-benzenediol	+	—	—
	2,5-Dimethyl-1,4-benzenediol	+	—	+
	2,3,5-Trimethyl-1,4-benzenediol	+	—	—
	4-Propyl-1,3-benzenediol	+	—	—
	2,5-Dihydroxyacetophenone	+	—	—
	2,3-Dimethyl-5-methoxyphenol	+	—	—
	2-Naphthol	+	—	—
	4-Hydroxypropiophenone	+	—	—

	3-(Bromomethyl)phenol	+	-	-
	2-Ethoxy-4-methylphenol	+	-	-
	2-Methyl-1-naphthol	+	-	-
	4-(3-Hydroxypropyl)-2-methoxyphenol	+	-	-
	3-Phenoxyphenol	+	-	-
	Tetrabromobisphenol A	+	-	-
Alkenes and hydrocarbons		0 specie	11 species	15 species
	1,1,2,2-Tetrachloroethylene	-	-	+
	(+)-alpha-Pinene	-	+	-
	3,7-Dimethyloct-1-ene	-	+	-
	1,4-Dichlorocyclohexane	-	+	-
	3,4-Dimethylheptane	-	-	+
	n-Decane	-	-	+
	n-Dodecane	-	+	+
	n-Pentatriacontane	-	+	+
	n-Tetradecane	-	+	+
	n-Triacontane	-	+	-
	n-Hentriacontane	-	+	-
	n-Hexadecane	-	+	+
	1-Undecylcyclopentane	-	-	+
	Hexatriacontane	-	+	+
	n-Octacosane	-	-	+
	n-Heptadecane	-	-	+
	n-Octadecane	-	-	+
	n-Tetracosane	-	+	+
	n-Eicosane	-	-	+
	N-nonacosane	-	-	+
Pyridine compounds		7 species	3 species	6 species
	Pyridine	+	-	-
	2-Methylpyridine	+	-	-
	4-Methylpyridine	+	-	-
	3-Methylpyridine	+	-	-
	2,6-Dimethylpyridine	+	-	-
	2,6-Diethylpyridine	+	-	-
	1,2,3,6-Tetrahydro-1-(1-oxobutyl)pyridine	+	-	-
	3-Hydroxy-2-methylpyridine	-	-	+
	3-Methyl-2(1H)-pyridinone	-	+	+
	5-Methyl-2(1H)-pyridinone	-	+	+
	6-Methyl-2(1H)-pyridone	-	+	-
	4-(Hydroxymethyl)pyridine	-	-	+
	2,6-Dimethyl-3-hydroxypyridine	-	-	+
	5H-Indeno[1,2-b]pyridine	-	-	+
Furan compounds		3 species	2 species	1 specie
	2,5-Dimethylfuran	+	-	-
	Tetrahydro-2,5-dimethylfuran	-	+	-
	3-Acetyl-2,4-dimethylfuran	+	-	-
	1,3-Dihydroisobenzofuran	-	+	-
	5-Hydroxy-2-methylbenzofuran	+	-	-
	2-Vinylbenzofuran	-	-	+
Quinolines		1 specie	0 specie	0 specie
	Quinoline	+	-	-
Thiophenols		1 specie	0 specie	0 specie
	4-Isopropylthiophenol	+	-	-
Acid and ester compounds		6 species	18 species	22 species
	9-Bromononanoic acid	+	-	-
	N-p-Toluenesulfonyltyrosine	+	-	-
	4-Nitrobenzoic acid-10-undecenylester	+	-	-
	Octadecyl-4-pyridinecarboxylate	+	-	-
	Octadecyl nicotinate	-	+	-
	5-Bromo-2-methoxybenzyl hexyl ester phthalicacid	+	-	-
	6-Methyl-2-pyridinecarboxylic acid	+	-	-
	Butanoic acid	-	+	+
	Pentanoic acid	-	+	+
	4-Hydroxypentanoic acid lactone	-	-	+
	Phenyl N-methylcarbamate	-	-	+
	Hexanoic acid	-	-	+
	(E)-3-Hexenoic acid	-	-	+

	4-Hexanolide	—	—	+
	Benzoic acid	—	+	+
	Ethyl 5-piperidino-4-ketocaproate	—	—	+
	2-Methylbenzoic acid	—	+	+
	3-Methylbenzoic acid	—	+	+
	4-Methylbenzoic acid	—	+	+
	3,4-Dimethylbenzoic acid	—	—	+
	3,5-Dimethylbenzoic acid	—	—	+
	Phenylacetic acid	—	—	+
	1-(2-Ydroxy-4-methoxyphenyl)-1-propanone	—	—	+
	2-Naphthoic acid	—	—	+
	Nonanoic acid, hexadecyl ester	—	—	+
	Methyl-4-hydroxyphenylacrylate	—	—	+
	Hexadecanoic acid	—	+	+
	Octadecanoic acid	—	+	+
	Bis(2-ethylhexyl) phthalate	—	—	+
	3-Methyl pentanoic acid	—	+	—
	4-Methyl-3-pentenoic acid	—	+	—
	Noratropine	—	+	—
	Methyl-6-(2-furoyl)hexanoate	—	+	—
	Benzoic acid, ctadecyl ester	—	+	—
	2-Methylphenyl isocyanate	—	+	—
	Ethyl 2-ethoxybenzoate	—	+	—
	3,4-Diaminobenzoic acid	—	+	—
	Butyl isobutyl phthalate	—	+	—
Aldehydes and ketones		3 species	10 species	13 species
	3-[3-(1-Ethyl-1H-pyrazol-4-yl)prop -2-enoyl]-2H-chromen-2-one	+	—	—
	3-Methyl-2-cyclopentenone	+	—	+
	2-(2-Hydroxyphenyl)-2,5-cyclohexadiene-1-4-dione	+	—	—
	4-Methyl-2-pentanone	—	—	+
	4-Hydroxycyclohexanone	—	—	+
	N-Methylpyrrolidone	—	+	+
	2-Piperidone	—	—	+
	1,5-Dimethyl-2-pyrrolidinone	—	—	+
	1-Methyl-2-pyridone	—	—	+
	3,6-DiMethyl-2(1H)-pyridinone	—	—	+
	1,3-Dimethyl-2(1H)-pyridone	—	—	+
	1,4-Dimethyl-2(1H)-pyridone	—	—	+
	2-Fluoro-6-trifluoromethylacetophenone	—	—	+
	(E)-4-Methoxycinnamaldehyde	—	—	+
	4-Biphenylcarboxaldehyde	—	—	+
	Doxapram	—	+	—
	4-Amino-3-penten-2-one	—	+	—
	1,4-Androstadien-3,17-dione	—	+	—
	3-Methyl-2,3-dihydrobenzofuran-2-one	—	+	—
	1,2-Benzodihydropyrone	—	+	—
	6-Hydroxycoumarin	—	+	—
	Pirenzepine	—	+	—
	3,4-Dihydro-9-methyl-2H-pyrido[1,2-a]pyrimidin-2-one	—	+	—
	2,2-Dibromocholestanone	—	+	—
Benzene compounds		7 species	3 species	9 species
	Allylbenzene	+	—	—
	1-(3-Methylbutyl)-2,3,4,5-tetramethylbenzene	+	—	—
	2,2'-Dimethoxy-3,3',5,5'-tetrabromobiphenyl	+	—	—
	2,2'-Dihydroxybiphenyl	+	—	+
	2,5-Dimethoxytoluene	+	—	—
	2,5-Dihydroxybiphenyl	+	—	+
	4,4'-Dihydroxybiphenyl	+	—	+
	Toluene	—	—	+
	Ethylbenzene	—	+	—
	1,3-Dimethyl-benzene	—	+	+
	1,4-Dimethyl-benzene	—	+	+
	1,2-Dimethyl-benzene	—	—	+
	1-Tert-Butyl-4-vinylbenzene	—	—	+
	7-Hydroxycadalene	—	—	+
PAHs		2 species	2 species	4 species
	Naphthalene	+	—	—



	2,7-Di-tert-butyl-naphthalene	—	+	—
	6-Methoxy-1,2,3,4-tetrahydronaphthalene	—	+	—
	1,4-Dihydro-1-methyl-1,4-epoxynaphthalene	+	—	+
	9-Methyl-S-octahydrophenanthrene	—	—	+
	1,2,3,4,5,6,7,8-Octahydro-9,10-dimethylantracene	—	—	+
	9,9-Dimethyl-2,7-dini tro-9H-fluorene	—	—	+
Piperidines		1 specie	0 specie	1 specie
	1-[3-(4-Tert-Butylphenyl)-2-methylpropyl]piperidine	+	—	—
	3,5-Dimethylpiperidine	—	—	+
Oxazine compounds		4 species	2 species	3 species
	Mesoridazine	+	—	—
	2,5-Dimethyl-6,7-dihydro-5H-cyclopentapyrazine	+	—	—
	2-Isopropenyl-3,6-dimethylpyrazine	+	—	—
	2-Isopropyl-3-methoxypyrazine	+	—	—
	Thioridazine	—	+	+
	10-[2-(1-Methylpiperidin-2-yl)ethyl]-2-(methylsulfinyl)-10H-phenothiazine	—	—	+
	2-Methyl-3-nitroindolizine	—	—	+
	2-Methoxypyrazine	—	+	—
Amines		3 species	3 species	8 species
	5-Methoxy-N,N-diallyl-1H-indole-3-ethanamine	+	—	—
	N-[(4-hydroxy-3-methoxyphenyl)methyl]-undecanamide	+	—	—
	3-Nitro-N-methylaniline	+	—	—
	N-Ethyl-N-methyl-2-propen-1-amine	—	—	+
	N,N-Diethyl-2-propen-1-amine	—	—	+
	N-Isopropylideneisopropylamine	—	—	+
	N-Ethylmaleimide	—	—	+
	Benzamide	—	—	+
	N,N-Dimethyl-6-(2-phenylethynyl)-2,1,3-benzoxadiazol-4-amine	—	—	+
	N-(2-Naphthyl)aniline	—	+	+
	N-(6,9-Dihydro-6-oxo-1H-purin-2-yl)hexadecanamide	—	+	—
	Erucylamide	—	+	+
Ethers		1 specie	0 specie	0 specie
	4-Ethylanisole	+	—	—
Alcohol compounds		3 species	3 species	0 specie
	5-Indanol	+	—	—
	1-Indanol	+	—	—
	6-Methyl-4-indanol	+	—	—
	2-Ethylhexanol	—	+	—
	1-(1H-Imidazol-4-yl)-2-tetradecylcyclobutanol	—	+	—
	4-Chromanol	—	+	—
Quinones		1 specie	0 specie	1 specie
	2,3,5,6-Tetramethyl-1,4-benzoquinone	+	—	—
	(2-Hydroxy-3-oxo-1,4,6-cycloheptatrienyl)-p-benzoquinone	—	—	+
Oxazoles		1 specie	0 specie	0 specie
	(20 $\beta$ )-16-[(1R)-2,3,4,9-Tetrahydro-1H-pyrido(3,4-b)indol-1-yl]-17-norcorynan	+	—	—
Imidazoles		1 specie	0 specie	1 specie
	2-Mercapto benzimidazole	+	—	—
	1,4-Dimethylimidazole	—	—	+
Pyrazoles		1 specie	0 specie	0 specie
	4-Methyl-3-phenyl-pyrazole	+	—	—
Others		3 species	5 species	5 species
	5-Formyl-2,4-dimethyl-1H-pyrrole-3-carbonitrile	+	—	—
	8-Azidoadenosine	+	—	—
	Cyclic octaatomic sulfur	+	+	—
	Hexathiane	—	+	—
	1,2-Phenylene diisothiocyanate	—	+	—
	N-(4-Hydroxy-2-methylcyclohexyl)-N'-(4-hydroxyphenyl)urea	—	+	—
	Camazepam	—	+	—
	2-Deoxy-D-ribose	—	—	+
	2,3-Dimethylmaleic anhydride	—	—	+
	4-Methoxyindole	—	—	+
	(2-Methoxy-5-methylphenyl)hydrazine	—	—	+
	1,4-Dihydro-6-methyl-2,3-quinoxalinedione	—	—	+

Note: (1) The similarity of each compound is more than 60% with NIST database; (2) — Not detected, + Detected; (3) Digital represents the number of types of compounds.

对比发现, MIBK 流程处理 COD 的效果较 IPE-PO 流程优, 根据萃余液 GC-MS 结果可知, IPE-PO 流程处理后 COD 主要由两部分组成, 即未被萃取污染物和溶解的萃取剂, 而 MIBK 流程有萃余液蒸馏步骤, 因此有必要对这两个流程处理过的废水进行生化处理, 全面考

察对废水的解毒能力。

### 3.3 生化处理萃余液结果

分别对两个流程处理后的萃余液进行生化处理, 处理装置如图 5 所示。



图 5 萃余液生化处理装置

Fig.5 The biochemical treatment device of raffinate

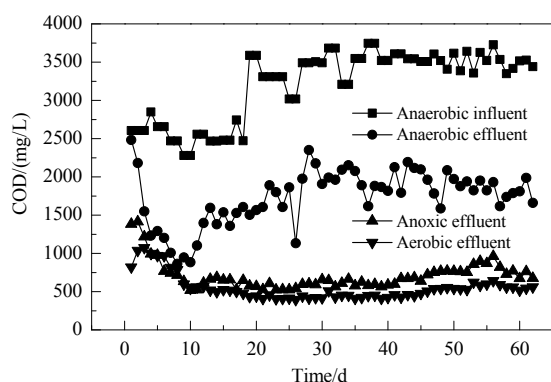


图 6 MIBK 流程处理后的废水经过生化处理结果

Fig.6 The biochemical treatment results of wastewater after treated by MIBK process

对 MIBK 流程和 IPE-PO 流程的萃余液按相同比例稀释后作为生化进水。生化流程为厌氧-缺氧-好氧, 总停留时间为 100~200 h, 其中厌氧停留时间 24 h, 缺氧停留时间 24 h, 好氧停留时间 80 h, 处理量为 430 mL/d, 进水流量为 0.3 mL/min, 处理温度 35 °C, 生化进水 pH=6.5~9, 处理时间 62 d, 各工段处理后 COD 结果见图 6 和 7。从图可见, 由于 MIBK 流程萃余液 COD 比 IPE-PO 流程低, 相应的, 生化进水 COD 浓度比 IPE-PO 低, 但厌氧处理后 COD 浓度区别不大。继续缺氧和好氧处理后, IPE-PO 流程好氧段出水 COD 浓度比 MIBK 流程低, 表明其出水可生化性好, 在预处理阶段比 MIBK 流程更能有效脱除有毒污染物, 少量溶于萃余液中的萃

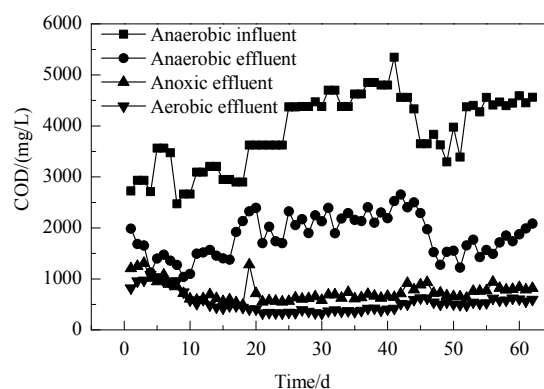


图 7 IPE-PO 流程处理后的废水经过生化处理结果

Fig.7 The biochemical treatment results of wastewater after treated by IPE-PO process

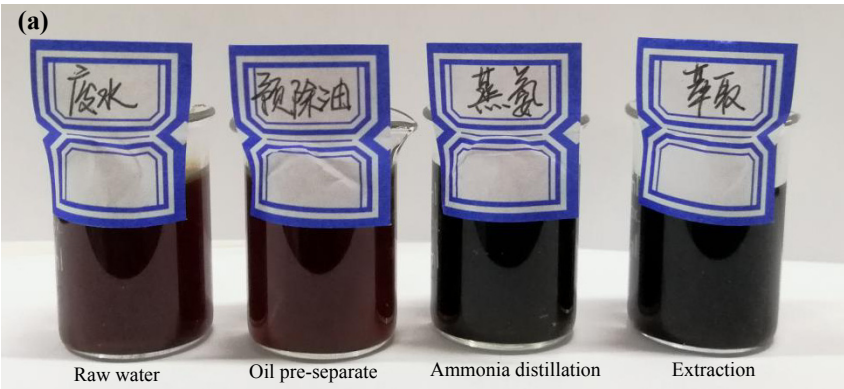
取剂易厌氧降解。尽管 IPE-PO 流程未经高能耗的蒸馏萃取剂步骤, 但污染物脱除率比 MIBK 流程高。

### 3.4 酚油共萃协同解毒技术处理煤化工废水

采用酚油共萃协同解毒技术和 IPE-PO 专用解毒萃取剂处理煤化工废水, 并分别对萃余液进行生化处理(厌氧、缺氧、好氧)和深度处理(混凝、催化氧化、膜生物反应器(MBR)), 废水经各工段处理后 COD 和 UV<sub>254</sub> 脱除效果见表 5, 水质见图 8。可看出经各工段处理后, COD 的去除率达 99.78%, UV<sub>254</sub> 去除率达 99.9%。水质颜色从深棕色变为无色, 最终出水 COD <100 mg/L, UV<sub>254</sub>=0.5 cm<sup>-1</sup>, 出水可排入污水场, 运行成本不超过 10 元/t。

表 5 煤化工废水经过各工段处理 COD 和 UV<sub>254</sub> 脱除结果  
Table 5 The COD and UV<sub>254</sub> removal results of coal chemical wastewater in various stages

Stage	COD/(mg/L)	Removal rate of COD/%	UV <sub>254</sub> /cm <sup>-1</sup>	Removal rate of UV <sub>254</sub> /%
Raw water	34230	—	197.41	—
Oil pre-separate	13632.2	60.17	102.06	48.30
Ammonia distillation	8940.71	73.88	54.07	72.61
Extraction	7637	77.69	35	82.19
Anaerobic	1643.6	95.2	16.8	91.49
Hypoxia	819.1	97.61	12.6	93.62
Aerobic	569.7	98.34	10.6	94.63
Coagulation	328.1	99.04	5.2	97.37
Catalytic oxidation	91.8	99.73	0.9	99.54
Membrane Bio-Reactor (MBR)	75.25	99.78	0.5	99.90



(a) The outflow of pretreatment stage



(b) The outflow of biochemical stage and advanced stage

图 8 各工段水质照片

Fig.8 Water quality photos of each stage

4 结 论

从全过程污染控制角度提出了酚油共萃协同解毒技术及用于该技术的专用萃取剂 IPE-PO，克服了煤化工高浓度废水高效脱酚和深度解毒的难题。与工业中应用广泛的传统处理工艺—MIBK 萃取体系相比，优势明显，得到以下结论：

- (1) 该技术对煤化工高浓废水解毒效果显著，对苯酚完全脱除，总酚和杂环/多环等高毒性污染物脱除率较传统处理体系显著提高，其中总酚去除率达 90%以上。
- (2) 该技术将废水中 101 种污染物降至 74 种，能高效脱除有毒污染物，大幅提高废水可生化性。深度处理后，COD 降至 100 mg/L 以下，满足污水场进水要求。

(3) 与 MIBK 萃取体系相比，用萃取剂 IPE-PO 处理后萃余液中因萃取剂少量溶解导致 COD 处理效果略差，但处理后废水可生化性好，减少了蒸馏萃余液的高能耗步骤，运行成本不超过 10 元/t。

参考文献

[1] 吴晓华, 宋二波, 贾尚伟. 基于 SWOT 分析的我国洁净煤技术发展研究 [J]. 洁净煤技术, 2015, 21(1): 24–28.  
Wu X H, Song E B, Jia S W. Research on development of clean coal technology China based on SWOT analysis [J]. Clean Coal Technology, 2015, 21(1): 24–28.

[2] 方芳, 韩洪军, 崔立明, 等. 煤化工废水“近零排放”技术难点解析 [J]. 环境影响评价, 2017, 39(2): 9–13.  
Fang F, Han H J, Cui L M, et al. Analysis on technological difficulties of near zero discharge for coal gasification wastewater treatment [J]. Environmental Impact Assessment, 2017, 39(2):

- 9–13.
- [3] Gai H J, Feng Y R, Lin K Q, et al. Heat integration of phenols and ammonia recovery process for the treatment of coal gasification wastewater [J]. Chemical Engineering Journal, 2017, 327: 1093–1101.
- [4] Zhu H, Han Y X, Xu C Y, et al. Overview of the state of the art of processes and technical bottlenecks for coal gasification wastewater treatment [J]. Science of the Total Environment, 2018, 637/638: 1108–1126.
- [5] Xu W C, Zhang Y X, Cao H B, et al. Metagenomic insights into the microbiota profiles and bioaugmentation mechanism of organics removal in coal gasification wastewater in an anaerobic/anoxic/oxic system by methanol [J]. Bioresource Technology, 2018, 264: 106–115.
- [6] Cui P Z, Mai Z H, Yang S Y, et al. Integrated treatment processes for coal-gasification wastewater with high concentration of phenol and ammonia [J]. Journal of Cleaner Production, 2017, 142: 2218–2226.
- [7] Xu P, Xu H, Zheng D Y. The efficiency and mechanism in a novel electro-Fenton process assisted by anodic photocatalysis on advanced treatment of coal gasification wastewater [J]. Chemical Engineering Journal, 2019, 361(1): 968–974.
- [8] Ji Q H, Tabassum S, Hena S, et al. A review on the coal gasification wastewater treatment technologies: past, present and future outlook [J]. Journal of Cleaner Production, 2016, 126: 38–55.
- [9] 钱宇, 周志远, 陈赟, 等. 煤气化废水酚氨分离回收系统的流程改造和工业实施 [J]. 化工学报, 2010, 61(7): 1821–1828.
- Qian Y, Zhou Z Y, Chen Y, et al. Process retrofit and industrial implementation of phenol and ammonia recovery from coal-gasification wastewater [J]. CIESC Journal, 2010, 61(7): 1821–1828.
- [10] Yang C F, Yang S Y, Qian Y, et al. Simulation and operation cost estimate for phenol extraction and solvent recovery process of coal-gasification wastewater [J]. Industrial & Engineering Chemistry Research, 2013, 52(34): 12108–12115.
- [11] 钱宇, 杨思宇, 马东辉, 等. 煤气化高浓酚氨废水处理技术研究进展 [J]. 化工进展, 2016, 35(6): 1884–1893.
- Qian Y, Yang S Y, Ma D H, et al. Research advances in treatment of coal gasification wastewater with high phenol and ammonia [J]. Chemical Industry and Engineering Progress, 2016, 35(6): 1884–1893.
- [12] Yang C F, Qian Y, Zhang L J, et al. Solvent extraction process development and on-site trial-plant for phenol removal from industrial coal-gasification wastewater [J]. Chemical Engineering Journal, 2006, 117(2): 179–185.
- [13] Wang Z X, Xu X C, Gong Z, et al. Removal of COD, phenols and ammonium from Lurgi coal gasification wastewater using A(2)O-MBR system [J]. Journal of Hazardous Materials, 2012, 235/236: 78–84.
- [14] Wang W, Han H J. Recovery strategies for tackling the impact of phenolic compounds in a UASB reactor treating coal gasification wastewater [J]. Bioresource Technology, 2012, 103: 95–100.
- [15] Tabassum S, Ji Q H, He N S, et al. Treatment of coal gasification wastewater by anaerobic SBR–aerobic SBR process for elimination of toxic organic matters—a lab scale study [J]. RSC Advances, 2015, 5: 58334–58344.
- [16] 何苗. 杂环化合物和多环芳烃生物降解性能的研究 [D]. 北京: 清华大学, 1995: 5–30.
- He M. A study on biodegradability of heterocyclic compounds and polycyclic aromatic hydrocarbons [D]. Beijing: Tsinghua University, 1995: 5–30.
- [17] 程能林. 溶剂手册 [M]. 北京: 化学工业出版社, 2007: 522–615.
- Cheng N L. Solvent handbook [M]. Beijing: Chemical Industry Press, 2007: 522–615.
- [18] 麦子豪. 煤气化高浓酚氨污水处理过程工艺设计与节能优化 [D]. 广州: 华南理工大学, 2016: 6–12.
- Mai Z H. Energy usage optimization and process design of the phenols–ammonia wastewater treatment processes [D]. Guangzhou: South China University of Technology, 2016: 6–12.