

电厂粉煤灰炭制颗粒活性炭的研究

吴新华 余 玮

(福建林学院林工系, 南平 353001)

摘要 以木炭或煤为辅助原材料, 采用预活化工艺, 将炭酸水洗后, 经活化或二次活化后制成颗粒活性炭。成品炭碘值为 600—700mg/g。在工业性试生产中, 新生产的活性炭碘值为 630—800mg/g, 耐磨强度超过 95%, 从而为粉煤灰综合利用开辟了新途径。

关键词 粉煤灰, 活性炭, 综合利用。

粉煤灰是以含 SiO_2 , Al_2O_3 , Fe_2O_3 , FeO , CaO 等为主要成分的固体废弃物, 其中含有 10%—22% 的未燃尽的炭粒。将粉煤灰炭制造活性炭不仅为活性炭生产提供原材料, 而且能为粉煤灰综合利用提供有效途径。利用粉煤灰炭制颗粒炭在国内曾有过报道^[1]。但尚未见其进行工业性生产。本课题以开辟粉煤灰综合利用新路为目的, 探索最佳工艺参数, 结合目前活性炭生产设备, 并进行工业性生产, 以期迅速投入生产, 创出效益。

1 原材料

粉煤灰炭分为精炭和中炭 2 种, 主要区别在于固定碳含量多少。据文献报道^[1], 粉煤灰炭挥发分低, 粒度细, 但从电镜上观察, 尚看不出已经燃烧的迹象, 因而是生产活性炭的潜在原料。

本次实验原材料取自福建省永安火电厂的中炭。其工业分析结果见表 1。经中国科学院福建物质结构研究所 X-射线衍射分析, 确定大部分物质为无定形碳, 有少量 SiO_2 晶体。经发射光谱分析, 确定还含有 Fe、Mg、Al、Ca 等元素。含硅量经江西省华东地质学院分析测定为 10.33%。

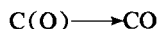
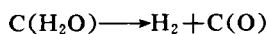
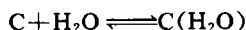
表 1 粉煤灰炭、木炭和煤的工业分析

炭类	灰分(%)	水分(%)	挥发分(%)	固定碳(%)
中炭	21.2	16.7	3.2	75.6
精炭	11.8	0.4	1.4	86.8
煤	21.2	11.3	12.0	66.7
木炭	9.6	8.4	2.9	87.5

2 活化机理

2.1 水蒸气活化机理^[2]

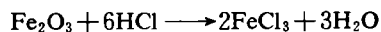
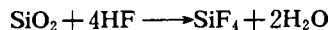
水蒸气作为活化剂用于制造活性炭, 这种方法称为气体活化法。由于炭粒在燃烧过程中表面形成残缺的微晶, 它们的化合价没有被相邻的碳原子所饱和, 因而比较活泼, 首先与水蒸气起反应:



当 CO 逸出后, 暴露出来的炭又成为活泼的反应中心, 如此不断反应, 其结果造成孔隙扩大, 新孔产生, 闭塞孔开放。当烧失率小于 50% 时, 就得到微孔活性炭。

2.2 预活化机理

由中炭的工业分析得知, 灰分含量为 16%, 而硅含量却占了 10.33% 之多, 可见比例之大。由于中炭富含在高温燃烧中形成的灰-炭连生体, 简单地利用酸水洗, 灰分去除量不大。灰-炭连生体的紧密结构, 使它们得以相互保护, 因此, 简单的酸水洗只能除去表面的灰分, 而内部仍然有大量的硅。预活化就是利用水蒸气, 使灰-炭连生体的联结力减弱, 整体结构处于松弛状态, 灰分便可以由表及里地除去。酸洗反应为:



结果发现, 含硅量为 3.4%。这样, 当活性炭灰分降低后, 吸附力便易于提高。

3 实验结果与讨论

经过探索性实验后,确定了活化反应的温度、时间、粘结剂的成分和用量。由于强度尚需进一步提高,因此,针对粉煤灰炭挥发分较低的特点进一步实验。

3.1 酸洗炭加助剂的实验

由于粉煤灰炭含灰分较高,有必要在粘结前进行酸水洗。实验的工艺条件及结果见表 2。

从表 2 中可以看出,酸水洗除去了粉煤灰的部分灰分后,使碘值有所提高。

H₃PO₄ 在药品活化法中作为活化剂^[2]在生

产中已经得到证实,它除了具有强酸性质外,在高温下,能呈熔融状态,易于在炭中渗透造孔,是提高活性的主要原因。

据文献报道^[3],KOH 可以作为助剂,促进活化。在实验中,由于设备密封不好,混入空气,活化反应过于剧烈,成品炭得率下降,而碘值没有提高。

辅助试剂的加入主要是为了提高碘值。而为了提高强度,则需加入煤粉或白炭等辅助材料,以利于二次活化,提高吸附性能。表 2 的实验数据也正体现了这一点。

3.2 预活化实验

表 2 酸洗炭加助剂实验结果

样品号	酸处理	辅助试剂	辅助材料	粘结剂 (%)	活化时间 (h)	产品性能			二次活化	
						碘值(mg/g)	强度(kg/条)	得率(%)	时间(h)	碘值(mg/g)
F9001	HF	H ₃ PO ₄	木炭(10%)	47	3	486		40.0		
F9002	HCl	H ₃ PO ₄	木炭(30%)	47	3	422		45.5		
F9003	HCl	CaCO ₃	无	47	3	512		40.0		
F9004	无	CaCO ₃	无	47	3	469		48.2		
F9005	无	H ₃ PO ₄	木炭(10%)	47	3	537		58.2		
F9006	无	H ₃ PO ₄	无	47	3	518		60.0		
F9007	无	无	白炭(20%)	40	3	374	7.6	82.2		
F9008	无	无	白炭(30%)	45	3	471	7.5	45.3		
F9009	无	无	白炭(30%)	50	3	469	8.6	39.5		
F9010	无	KOH(5%)	木炭(20%)	45	3	411		60.6		
F9011	无	KOH(3%)	木炭(30%)	47	3	359		20.2		
F9012	无	KOH(3%)	木炭(30%)	47	3	348		32.2		
F9013	HCl	无	煤(30%)	47	3.5	440			1.5	560
F9014	HCl	无	煤(20%)	47	3	400			3	518

表 3 预活化实验结果

样品号	预活化条件(水蒸气,950℃)	酸处理	煤(%)	一次活化条件(950℃)	碘值(mg/g)	二次活化条件	碘值(mg/g)
F9401A	固定床,2h	HCl	无	6h	548		
F9401B	固定床,2h	HCl+HF	无	6h	606		
F9402A	固定床,6h	HCl	无	5h	518	950℃,2h	669
F9402B	固定床,6h	HCl+HF	无	5h	604	950℃,2h	765
F9403A	回转炉,3h	HCl	无	3h	507		
F9403B	回转炉,3h	HF	无	3h	521		
F9403C	回转炉,3h	HCl+HF	30	4h	547		
F9403D	回转炉,3h	HCl+HF	无	2h	498		

预活化实验主要在回转炉和固定床中进行。实验的工艺条件和结果见表 3。

从表 3 可以看出,预活化对产品吸附性能的

提高作用显著。最高值可以达到 765mg/g。盐酸和氢氟酸的预处理效果也不错。另外,活化时间的延长对吸附性能也有所提高(表现在二次活化

中)。

4 工业性试生产

根据实验室小试的工艺条件,我们在福建省浦城林化厂和建阳第二化工厂进行了工业性试生产。预活化在焖烧炉中进行,温度 500—600℃,24h。炭化在焖烧炉中进行,温度 500—600℃,24h。活化在多管炉中进行,温度 850—900℃,12—24h。中炭分酸洗和未酸洗 2 种。实验结果见表 4。

表 4 试生产实验结果

样品号	一次活化		二次活化		备注
	碘值 (mg/g)	碘值 (mg/g)	耐压强度 (kg/条)	耐磨强度 (%)	
F9501A	445	578	>10	95	未酸洗
F9501B	488	644	>10	95	未酸洗
F9501C	500	637	>10	95	未酸洗
F9502	560	800	>10	90	酸洗

从表 4 中可以看出,在现有工艺条件下,粉煤灰炭制颗粒炭的产品指标已达到了国家标准,而且比小试结果要好。这是因为工厂中采用四柱液压机挤条,炭条韧性极好,产品强度高,适于长

时间活化,有利于碘值的提高。

5 结论

(1)用电厂粉煤灰炭生产活性炭其最佳工艺为:以木炭为辅助材料,粘结剂用量 40%,炭化温度 600℃,活化温度 950℃,时间均为 24h。

(2)活性炭碘值为 600—800mg/g,其余各项指标均达到国家标准。完全适用于空气净化、工业用水处理、废水处理等领域。

(3)本工艺可以采用现有颗粒炭生产设备,技术可行,成本低效益高。不仅为活性炭生产扩大了原材料,而且为粉煤灰综合利用解决了一大难题,社会、经济效益显著。

致谢 本课题得到浦城林化厂、建阳二化领导和同仁的支持,福建林学院林化 89 届、90 届和 92 届共 12 位同学协助工作。特此表示最诚挚的谢意。

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than 0.5 mg/L, i. e., the national standard for its discharge.

Key words: acidic wastewater, pollution control, arsenic (As), iron salts neutralization.

Study on the Manufacture of Activated Carbon from the Carbon in Coal Ash from a Power Station. Wu Xinhua and Yu Wei (Fujian College of Forestry, Nanping 353001); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 47—49

A production process of activated carbon in which the carbon in a coal ash from a power station was used as a starting material has been developed. The optimized conditions for this process to produce a granular activated carbon were using charcoal, white charcoal or coal as an auxiliary raw material, together with which the starting material was undergoing a treatment in a preactivation process, then was washed with acid and water, and finally was activated or even further reactivated if required. The activated carbon product thus produced had an iodine value of 600—700 mg/g. The activated carbon from a pilot industrial production had an iodine value of 630—800 mg/g with a wearability of over 95%. This process provides a new way for coal ash to be utilized comprehensively.

Key words: coal ash, activated carbon, comprehensive utilization.

Comparative Study on the Capacities of Aerobic and Anaerobic Immobilized Microbes to Treat Organics. Wu Xiaolei et al. (Dept. of Environ. Eng., Tsinghua University, Beijing 100084); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 50—52

Activated and anaerobic sludges were respectively immobilized with polyvinyl alcohol (PVA) used as an entrapping agent, and then the immobilized sludges were separately used to degrade the organics in wastewater under the aerobic and anaerobic conditions, respectively. Comparisons in the capacity of treating organics were also made between the immobilized and free sludges and between the immobilized activated sludge and the immobilized anaerobic sludge. The results show that the volumetric loading was 1.3 to 2.1 times that of free sludge, meant by that the immobilized sludges had a higher capacity of treating organics than a free sludge. Under the conditions studied, the volumetric loading ratio of the immobilized anaerobic sludge to the free anaerobic sludge (2.13) was much higher than that of the immobilized activated sludge to the free activated sludge (1.30—1.54). Considering the sludge loading and gas yield per unit of sludge by weight, it was concluded that the capacity of microbe treating organics could be further developed in the immobilized anaerobic sludge so that the immobilized microbes entrapped in a gel would be more suitable for the anaerobic treatment of a high strength organic wastewater.

Key words: immobilized microbes, immobilized

activated sludge, immobilized anaerobic sludge, treating capacity.

Study on the Indicators for Evaluating the Activity of Immobilized Microorganism in the Degradation of Isocarbophos. Zhang Xiaohe et al. (Institute of Environmental Medicine, Tongji Medical University, Wuhan 430030); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 53—55

The indicators for evaluating the performance of immobilized microorganism before and after the biodegradation of isocarbophos in water samples have been studied. It has been found that the levels and degradation rates of the organophosphorus pesticide in water were in highly positive correlation to COD_{Cr} and COD_{Cr} removal, respectively, so that it would be proper to choose COD_{Cr} removal as a routine indicator for evaluating the activity of immobilized microorganism in the degradation of this pesticide. What was given in this article also included the regression equations established on the basis of experimental data, and the results from their significance tests, wherein the correlative coefficients of Eqs. 1—4, Eqs. 5 and 7, Eqs. 6 and 8, and Eqs. 9—12 were 0.992, 0.940, 0.951 and 0.978, respectively.

Key words: Isocarbophos, immobilized microorganism, biodegradation, indicators for evaluating activity.

Speciation of Selenium in Soils. Lan Yeqing et al. (Dept. of Basic Courses, Nanjing University of Agriculture, Nanjing 210014); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 56—58

The distribution of natural and applied selenium (Se) species in three kinds of soil, i. e., tide-saline soil (C), gray tide-soil (G) and yellow brown soil (Y), in Jiangsu province was studied. The results show that the naturally occurred Se species were mainly distributed as residual species (F_5), and F_5 in each of the three kinds of soil accounted for about 80% of total Se species. After an incubation for 4 months, the applied Se species were relatively homogeneous to be distributed as soluble species (F_1) (except in Y), exchangeable species (F_2), aqueous ammonia extractable species (F_3) and residual species (F_5). With two different treatments, the distribution of Se species was found to be in some relation to soil pH value, glutinous grains and free iron oxide levels. The soil pH value was in such an order as $C \approx G > Y$; the levels of glutinous grain and free iron oxides; $Y > C > G$; the percentage levels of F_1 and F_2 : $C \approx G > Y$; and the percentage levels of F_3 and F_5 : $Y > C > G$.

Key words: selenium (Se), soil, species.

Preliminary Analysis of Design Flow for Allowable Discharge Capacity of Rivers. Zheng Yingming (Institute of Environ. and Water Conservancy, Hehai University, Nanjing 210024); *Chin. J. Environ. Sci.*, **15**(4), 1994, pp. 59—61