

纳米材料 ZrO_2 颗粒液相吸附去除联苯胺研究

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摘要 通过静态试验方法研究了 ZrO_2 纳米颗粒液相吸附联苯胺的性能,结果表明,虽然联苯胺均可与 ZrO_2 纳米颗粒表面羟基及水分子形成氢键,但它与 ZrO_2 纳米颗粒表面羟基之间形成的氢键稍强,吸附去除效果较好,该吸附体系很好吻合 Freundlich 和 de Boer-Zwicker 吸附等温式,热分析显示联苯胺与 ZrO_2 纳米颗粒表面之间的吸附成键作用较弱。

关键词 ZrO_2 纳米颗粒 联苯胺 液相吸附

1 引言

本研究的目的在于探索纳米材料对有机、有毒、有害物质的吸附性能,通过试验得到所选纳米材料对所选吸附质的吸附参数及吸附机理,从而确定纳米材料在水处理中的吸附规律和应用范围。

2 试验方法

采用静态吸附实验方法。 ZrO_2 纳米颗粒由华东理工大学提供, ZrO_2 为四方晶型、白色粉末、平均粒径 25 nm,比表面积 $50 \sim 60 \text{ m}^2/\text{g}$ 。试验过程为:首先,称取一定量的 ZrO_2 纳米颗粒、放入烘箱中,在 105℃ 下活化 4 h,然后,取出活化后的 ZrO_2 纳米颗粒加入二次蒸馏水 10 mL,进行超声波振荡,使得 ZrO_2 纳米颗粒充分地

分散成乳状液。再加入配制成一定浓度的联苯胺溶液,在 30℃、pH=7.0 条件下进行恒温振荡实验,经过一定时间后,取出振荡混合液进行固液分离,固液分离和吸附质浓度测定在 1~2 min 内完成,避免分离时试验条件的变化而带来实验误差。

3 试验结果分析

3.1 吸附速率曲线

ZrO_2 纳米颗粒液相吸附联苯胺速率曲线见图 1,从图中可以看出对于联苯胺水溶液,在起始浓度 28 mg/L,35 mL 溶液中投加 50 mg ZrO_2 纳米颗粒时,平衡时间约在 30 min 左右,平衡时吸附质浓度为 11 mg/L,该条件下 ZrO_2 粉末吸附容量为 11.9 mg/g,

表 3 高效菌 PACT(厌氧)处理染料废水的运行效果

厌氧	处理水量	停留时	水温	$COD_{Cr}/\text{mg L}^{-1}$		COD_{Cr}	pH
160 d	L h^{-1}	间/h	/	进水	出水	去除率 %	
范围	7.2~13.5	8~15	24~32	960~700	442~755	20~40	6.5~8.0
平均	10.2	12	26	816	600	30	7.5

表 4 高效菌 PACT(好氧)处理分散染料废水的运行效果

好氧	处理水量	停留时	DO/	水温	$COD_{Cr}/\text{mg L}^{-1}$		COD_{Cr}	pH
160 d	L h^{-1}	间/h	mg L^{-1}	/	进水	出水	去除率 %	
范围	7.2~13.8	7~11	2~4	24~32	442~755	86~140	70~87	6.5~8.0
平均	10.2	8	3	26	600	110	80	7.5

7 结论

PACT 工艺通过半年的运行,控制以下影响因素在一定范围内,PACT 工艺运行效果较好。

(1) PACT 工艺具有耐负荷冲击能力,但生化进水的 COD_{Cr} 值不宜过大,一般在 1 000 mg/L 左右为好。

(2) 染色废水色度越高,含有毒成分越多,进水色

度最好控制在 500 倍以下。

(3) PACT 工艺进水 pH 值范围,一般控制在 6.5~8.5 左右为宜。

(4) 生化池内最佳温度为 25~30℃。

(5) 水力停留时间厌氧不 < 12 h,好氧不 < 7 h,处理效果较好。

(6) 好氧池溶解氧保持在 2~4 mg/L 范围内。

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吸附去除率为 61 %。

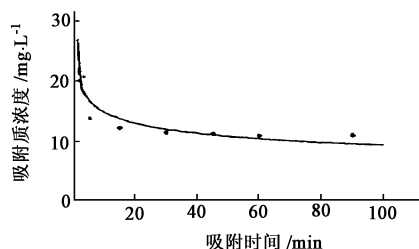


图1 ZnO₂ 纳米颗粒吸附联苯胺速率曲线

纳米颗粒吸附水中有机污染物质时,吸附剂与吸附质之间存在吸引或排斥的3种作用力,吸引力分2种,一种为库仑作用力,另一种吸引力为化学作用力,第3种作用力为斥力。

ZnO₂ 是典型的离子晶体,Zr⁴⁺ 具备高正电性,颗粒表面羟基化以后表现为一定的酸性,联苯胺分子中含有2个氨基,它们可与ZnO₂ 纳米颗粒表面羟基及溶剂水分子之间形成微弱的氢键,联苯胺与颗粒表面羟基形成的氢键要稍强于与水分子形成的氢键。

3.2 吸附等温线

根据平衡浓度和所投加吸附剂量数据,测得ZnO₂ 粉末吸附联苯胺的吸附等温线见图2。

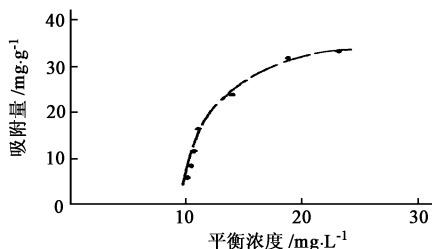


图2 ZnO₂ 纳米颗粒吸附联苯胺等温线

采用常用等温式对图2数据进行拟合,发现Freundlich和de Boer-Zwicker公式拟合效果最好,拟合曲线见图3和图4。

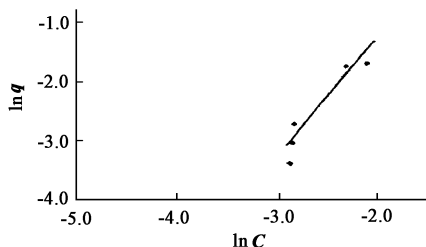


图3 ZnO₂ 吸附联苯胺等温线 Freundlich 拟合曲线

本研究条件下的吸附方程由拟合结果可表示为 Freundlich 公式:

$$q = 14.9 C^{1/0.499} \quad (1)$$

式中 q ——吸附容量; C ——吸附平衡浓度。

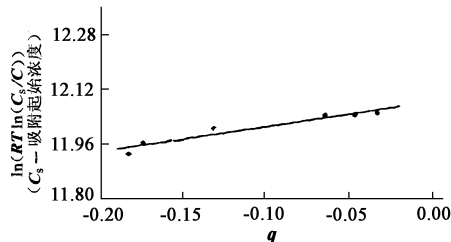


图4 ZnO₂ 吸附联苯胺等温线 de Boer-Zwicker 拟合曲线

或 de Boer-Zwicker 公式:

$$\ln(1/C) = 4.39 \times 10^{-9} \cdot e^{-0.748q} \quad (2)$$

式中 q ——吸附量; C ——吸附平衡浓度。

3.3 热分析结果

为了研究纳米材料与联苯胺之间的成键情况,探索纳米材料与有机吸附质之间的吸附机理,试验进行了吸附剂吸附吸附质以后的热分析研究。

在 52 附近 ZnO₂ 纳米颗粒有一脱水失重过程,这一阶段失重明显,以后平台逐渐向下偏,即为表面羟基逐渐脱附所致,失重量约占 1 %,ZnO₂ 吸附联苯胺的热重曲线,在 41 有一脱水失重过程与 ZnO₂ 粉末本身类似,另在 381 有一明显失重,失重时温度比联苯胺 128.7 的凝固点温度高,接近沸点温度,这说明联苯胺与 ZnO₂ 粉末表面羟基形成的氢键键合作用仍较弱。

4 结论

(1) 常用的气相吸附等温式中, Freundlich 和 de Boer-Zwicker 公式很好适合本研究试验条件,分别得出 30 条件下,ZnO₂ 纳米颗粒液相吸附联苯胺的 Freundlich 公式和 de Boer-Zwicker 公式分别为:

$$\text{Freundlich 公式: } q = 14.9 C^{1/0.499}$$

$$\text{de Boer-Zwicker 公式: } \ln(1/C) = 4.39 \times 10^{-9} \cdot e^{-0.748q}$$

(2) 从热分析曲线可知,联苯胺在纳米 ZnO₂ 颗粒表面既不是简单的类似凝聚的过程,也没有形成强有力的成键作用。

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STUDY ON THE REMOVAL OF BENZIDINE BY ADSORPTION IN THE AQUEOUS SOLUTION USING ZrO_2 NANOMETER POWDERS AS ABSORBENT Yang Dianhai *et al* (22)

Abstract The adsorption effect of benzidine on ZrO_2 nanometer powders in the aqueous solution is studied. The results show that hydrogen bond can be formed by benzidine and hydroxyl group or hydrone on the surface of ZrO_2 powders ,but the one by benzidine and hydroxyl group is slightly stronger than the one by benzidine and hydrone ,the removal efficiency is about 61 %. The adsorption system can be well in accord with isothermal equations of Freundlich and equation de Boer-Zwicker. The thermogravimetric and differential thermal analyses demonstrated that there has a weak adsorption between benzidine and nanometer powder.

Key words ZrO_2 nanometer powders , benzidine and liquid adsorption

PROJECT OF TREATING CASSAVA CITRIC ACID WASTEATER BY ANAEROBIC PROCESS

..... Guo Yongfu *et al* (24)

Abstract The system of wastewater treatment of a citric acid plant of Jiangsu ,which uses cassava as its main raw material after reconstructing the ferment jar as UASB. The results show that when the temperature of the influent keeps 38~42 and the COD_{Cr} is less than 1 000 mg/L ,the removal rate of COD_{Cr} is up to 95 % , and the organic loading (COD_{Cr}) is 9 $kg/m^3 \cdot d$. The granulation of anaerobic sludge is realized. Some experience and data were acquired in the practice ,which may be a reference for design or operation of UASB reactor.

Key words cassava , citric acid , anaerobic reactor UASB and wastewater treatment

TREATMENT OF TEXTILE COMPREHENSIVE WASTEWATER BY HYDROLYTIC ACIDIFICATION-BIOLOGICAL CONTACT OXIDIZATION-BLEACHING AND DECOLORATION PROCESS Xiao Yunan *et al* (27)

Abstract The conditions of the textile comprehensive wastewater discharged by Yida Textile Limited Company are as below :pH 10~14 , COD_{Cr} 1 000 ~ 1 500 (mg/L) , BOD_5 300 ~ 450 (mg/L) ,SS 300 (mg/L) , S^{2-} 3 (mg/L) ,wastewater temperature between 40 and 50 and its colority ranging from 400 to 600 times. The effluent is controlled within the discharging standards by using hydrolytic acidificationbiological contact oxidization-bleaching and decoloration process. After operation for more than two years ,the operational result has shown that the effluent quality keeps stable.

Key words textile comprehensive wastewater , hydrolytic acidification , biological contact oxidation , bleaching and decoloration.

TREATING WASTEWATER OF REGENERATIVE PAPER FROM WASTEPAPER USING BIOCHEMICAL PROCESS Hu Xuelian *et al* (30)

Abstract The composition and property of a regenerative paper-making wastewter are demonstrated ,whose treating technology is also analyzed and evaluated through typical engineering examples. Finally it is pointed out that a treatment with a biochemical method being its main process can control effectively the regenerative paper-making wastewater.

Key words regenerative paper-making wastewater , property of wastewater , biochemical process and chemical process

RESEARCH ON OPTIMAL SLUDGE LOADING OF TREATING BREWERY WASTEWATER BY HIGH CONCENTRATION ACTIVATED SLUDGE PROCESS Xing Yi *et al* (32)

Abstract In the article the scope of the optimal sludge loading is studied through experimentation in the treatment of brewery wastewater by high concentration activated sludge process. The SAS software system is used to analyze the test data and build a mathematical model ,which is verified by practical engineering data.

Key words high concentration activated sludge process ,brewery wastewater treatment , sludge loading , optimal sludge loading and sludge concentration

THE STUDY ON THE CLEANING PERFORMANCE OF CARTRIDGE DUST COLLECTORS

..... Wu Lirui *et al* (36)

Abstract Four types of filter cartridges are studied on their cleaning performance. The results show that the included angle of a filter cartridge has great influence on its cleaning performance. If the included angle is smaller than a certain value ,online cleaning is almost useless and off-line must be carried out. Moreover ,it is found that the cleaning effect is different at different part of a filter cartridge ; the worst effect takes place at the upper part. The reason is analyzed and measures are given to improve the effect.

Key words included angle of a filter cartridge , cleaning and off-line cleaning