用CARIX工艺去除饮用水中硝酸盐的改进研究

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摘要 针对硬度低而硝酸盐含量高的原水，采用阴离子交换柱研究了用改进型CARIX工艺提高对地下水中硝酸盐的去除. 除盐过程中，水中硝酸根和硫酸根等阴离子被碳酸氢根离子置换；再生阶段，用二氧化碳和氧化镁粉末，使树脂转变为重碳酸盐型. 结果表明，再生时加入氧化镁粉末能明显改善阴树脂的再生效率，最佳投加量为0.4%. 本树脂再生后硝酸盐去除率能达到50%以上.

关键词 CARIX工艺，硝酸盐，二氧化碳，饮用水.

硝酸盐污染的饮用水严重危及健康，寻求经济可行的饮用水的除硝酸盐技术已成为当务之急. CARIX工艺[1](二氧化碳再生离子交换树脂)采用一个由游离酸型弱酸阳树脂和重碳酸盐型强碱阴树脂所组成的混床，使溶解盐和碳酸交换. 混床树脂失效后，用CO_2同时再生2种树脂使树脂上的盐溶于水中，反应与产水相反. 改进型CARIX工艺用MgO代替$CaCO_3$作为化学添加剂，将少量MgO加到饱和的CO_2溶液中，即可产生一定浓度的$Mg(HCO_3)_2$溶液，从而大大提高了HCO_3^-浓度.

1 实验系统

采用北京市昌平县南口镇的地下水作为原水水源，水质情况见表1.

表1 南口地下水水质及国家饮用水标准/mg·L^{-1}

总硬度($CaCO_3$计)	pH	Cl^-	SO_4^{2-}	NO_3^-(N计)	HCO_3^-($CaCO_3$计)	TOC
295	7.74	27.4	47.0	22.3	175.8	0.1
450	6.5—8.5	250	250	20		

1.1 实验装置

如图1所示由3部分组成：水系统、气系统和水气混合系统. 水路部分：由压缩泵将再生剂容器内的再生剂打循环. 气路部分：CO_2气体由钢瓶经气体流量计流入再生剂容器中，溶于水形成再生液. 水气混合部分：循环流动的含CO_2水溶液，在预定压力下达到饱和后，由离子交换柱底部通入，上部流出，再生废液的流量由电磁阀来控制，它在预定的时间间隔内定时开启.

离子交换树脂装在一内径50 mm，高1000 mm的不锈钢交换柱中. 阴树脂装填量为1000 ml(羟型)，径高比为10. 在阴柱前串联一个阳柱，作为过滤器，可以避免铁离子的干扰以及有机物或胶体状无机物的污染. 本实验中采用D 110树脂作为保护柱.

1.2 工艺流程

(1) 产水 利用自来水管网水压，先使原水流入阳离子交换柱内，再从柱底流入阴离子交换柱内，流量均控制在10 L/h.

(2) 再生 再生时切断阴柱和阳柱之间的联接，仅再生阴柱. 再生剂的用量为15倍床体积，用压缩泵将再生剂循环20 min. 然后逆流

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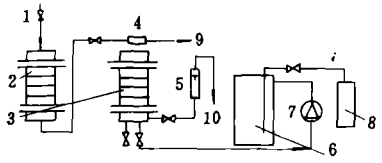

图1 实验装置

1. 原水 2. 阳离子交换柱 3. 阴离子交换柱 4. 电磁阀 5. 流量计 6. 再生剂容器 7. 循环泵 8. 二氧化碳钢瓶 9. 废再生液 10. 产水

通入交换柱内，使树脂恢复交换能力. 在再生废液出口处安装一电磁阀，闭阀 1 min，开阀 2 s，按此周期到再生废液排完为止. 总的再生时间约为 3 h.

(3) 逆流淋洗 再生剂用过以后，树脂层中夹带的剩余再生剂必须淋洗干净，附着的空气及 CO_2 气体必须赶出，为了减少淋洗水量，当再生剂流完时，将废液从柱底阀门全部排干，然后再反冲洗，淋洗水量为 3—5 倍床体积. 在每一轮实验中，产水与再生循环至少要重复进行 2 次以上，直到 2 次穿透曲线和 2 次再生曲线基本重复不变为止. 根据国内外的一些经验，本实验选定的 CO_2 分压为$(5.5—5.8)\times10^5$ Pa，本实验选用德国 Bad Rappenau 水厂和 Kilckberg 水厂采用的阴树脂 Amberlite IRA-458.

2 实验方法

2.1 树脂的预处理

离子交换树脂的工业产品中常含有多种杂质，使用前必须进行预处理，在小型交换柱内，先用水使树脂充分膨胀，然后用酸和碱交替处理 2 次(包括静态和动态再生).

2.2 提高阴树脂再生效率的实验

研究不同 MgO 添加量对再生效率的影响及最佳条件的选择. 再生时分别将不同重量的 MgO 粉末加入再生液中，配成 0.1%、0.2%、0.3%、0.4%、0.5%的 MgO 悬浊液，充入 CO_2 气体，在整个再生循环中；压缩泵一直在回路内打循环. 再生剂的循环导致了一个流动的交换床，阻止镁型化合物沉淀和再生过程中 $CaCO_3$、$CaSO_4$ 沉淀引起的树脂结垢现象. 当液相被 CO_2 饱和以后，仅仅需要从 CO_2 贮罐中补充少量 CO_2. 此量是在再生时被离子交换过程本身所消耗的量. 同时，分别与仅用 CO_2 再生和 $CaCO_3$ 作添加剂再生的情况作对比. NO_3^- 分析用美国 Orion 公司 EA940 多用离子计.

2.3 实验指标

再生剂用量一定时，以单位树脂上的洗脱量作指标[3]，能反映出再生效率的高低，主要体现在流出液水质和树脂的工作交换量. 由于本实验只考查 NO_3^- 的去除情况，树脂去除 NO_3^- 的工作交换容量可用穿透容量来表示，当树脂层高度一定，产水和再生的流速等操作条件一定，出水 NO_3^- 允许浓度均为 1.43 mmol/L，而各次实验的原水水质稍有不同，综合考虑各因素，本文采用 NO_3^- 的平均去除率作为衡量水处理效果的参考标准.

3 实验结果与讨论

3.1 Mg^{2+}浓度的变化

在一定范围内，增加 MgO 投加量，反应生成的 Mg^{2+} 增加. 当 MgO 浓度增加到一定(0.3%)时，溶液中 Mg^{2+} 变化不大. 0.4%和 0.5% MgO 条件下，Mg^{2+} 几乎不变(见图 2)，$CaCO_3$ 作添加剂测得的再生剂溶液中 Ca^{2+} 浓度变化曲线如图 3 所示. 与图 2 相比可知，再生过程中投加量相同，再生剂溶液中的 Mg^{2+} 浓度比 Ca^{2+} 浓度高出 10 倍以上. 因此，MgO 的效率高

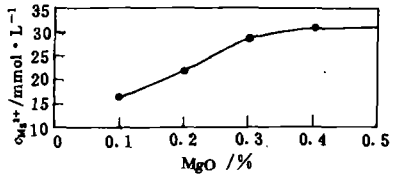

图2 再生剂溶液中 Mg^{2+} 浓度随 MgO 投加量的变化

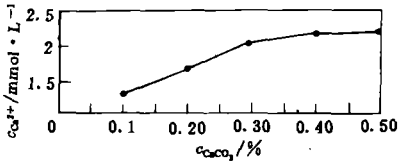

图3 再生剂溶液中 Ca^{2+} 浓度随 $CaCO_3$ 投加量的变化

于$CaCO_3$.

3.2 再生曲线的展开情况

图 4 为再生系统中投加不同重量的 MgO 粉末后 NO_3^- 浓度的展开曲线. 再生剂流过失效的树脂床，树脂上吸附的 SO_4^{2-}、NO_3^- 被 HCO_3^- 置换下来. NO_3^- 浓度经过最大值以后，浓度开始降低并趋于稳定.

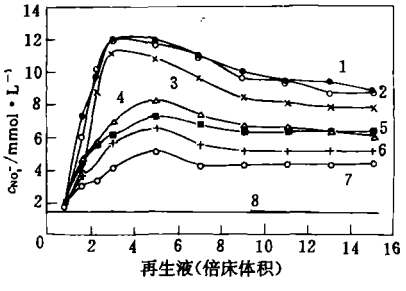

图 4　458 树脂再生期间的浓度展开曲线
(再生压力为(5.5—5.8)×10^5 Pa)
1. MgO 0.5%　2. CO_2　3. MgO 0.3%
4. MgO 0.2%　5. MgO 0.1%　6. $CaCO_3$ 0.3%
7. MgO 0.4%　8. NO_3^--(R)

3.3 穿透曲线分析

图 5 为产水中的 NO_3^-、SO_4^{2-} 浓度随产水量变化的关系曲线. 当含有 NO_3^-、SO_4^{2-} 的原水流经阴离子交换柱时，由于阴树脂对水中阴离子的亲合力不同，选择顺序为：$SO_4^{2-} > NO_3^- > HCO_3^-$，故产水中 SO_4^{2-} 的去除效果高于 NO_3^- 的去除效果.

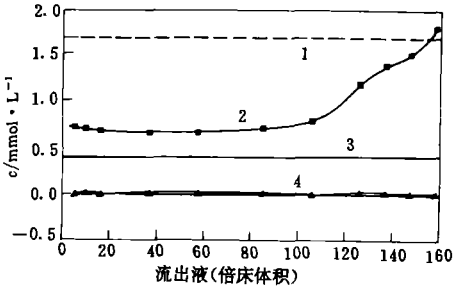

图 5　产水中 NO_3^- 和 SO_4^{2-} 浓度展开曲线
(再生剂：CO_2+0.3% MgO)　1. NO_3^--(R)
2. NO_3^-　3. SO_4^{2-}　4. SO_4^{2-}-(R)

3.4 NO_3^- 的去除率

表 2 为 458 树脂用不同的再生剂再生后的产水情况，从表 2 可知，CARIX 工艺中，仅用 CO_2 再生，阴树脂的再生效率较低. 而用 CO_2 和添加剂($CaCO_3$ 或 MgO)再生，会产生 $Ca(HCO_3)_2$或 $Mg(HCO_3)_2$，提高了再生剂溶液中 HCO_3^- 的浓度，使转化为重碳酸盐型的阴树脂份额增加. 而用 MgO 作添加剂的再生效果更好.

表 2　458 树脂再生后产水情况

再生剂	NO_3^- 的穿透容量 /mmol·L^{-1}	产水量 BV	出水平均 NO_3^- 浓度/mmol·L^{-1}	平均去除率/%	
				SO_4^{2-}	NO_3^-
CO_2	19.7	62	1.24	87.4	20.4
0.3% $CaCO_3$+CO_2	63.5	97	1.0	97.2	39.6
0.1% MgO+CO_2	81.9	112	0.83	96.0	47.0
0.2% MgO+CO_2	113.8	127	0.76	91.5	54.2
0.3% MgO+CO_2	130.0	140	0.72	93.4	56.2
0.4% MgO+CO_2	157.9	162	0.68	95.5	59.0
0.5% MgO+CO_2	159.5	163	0.67	96.6	59.2

4 结论

(1) 要提高 CARIX 工艺对硝酸盐的去除，必须改善阴树脂的再生效率. 再生阶段加入碳酸钙或氧化镁粉末能提高再生效率，但投加氧化镁粉末的效果更明显.

(2) 只采用阴离子交换柱时，必须用碳酸钙和氧化镁作再生剂.

(3) 最佳的氧化镁投加量为 0.4%. 进口树脂 Amberlite IRA 458 的产水情况：NO_3^- 可以从 23.6 mg/L 降到 8 mg/L(以 N 计). 平均去除率为 59.0%. 产水量为 162 倍床体积.

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The experiment was conducted in a vertical reactor with a total length of 3.5 m and cross section of 150 mm×150 mm to simulate flue gas desulfurization with lime and carbide lime slurry injection in the duct. Effects on So_2 removal were found, of such as the approach to adiabatic temperature at the exit, molar ratio of Ca to S, flux ratio of atomizing gas and slurry, gas inlet temperature, SO_2 initial concentration and gas residence time. Also, it was showed experimetally that SO_2 removal can achieve 65% at $\Delta T = 18$℃ and Ca/S = 1.5. In addition, a reaction model was developed, i.e., $\eta = 1 - [(T_i - T_{as})/(T_0 - T_{as})]^{-\frac{\alpha\beta}{\beta+R}}$, where α and β as equation parameters were determined by the conjugate gradient optimization method, and model predictions agree well with the experimental values with relative errors lower than 7%.

Key words: duct slurry injection, flue gas desulfurization, atomization.

Design of an Annular Denuder to Measure Atmospheric Ammonia. Tian Honghai et al. (Peking University, Beijing 100871): *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 20—23

A new trace gases sampler, annular denuder (AD), was developed and evaluated for the first time in China. Theoretical consideration was given and quality tests have been executed for designed AD. Its absorption efficiency for ammonia is over 97% and the detection limit is down to 0.15 $\mu g/m^3$ (10 m^3 sample volume). The intercomparisons of AD with filter pack as well as wet AD methods showed good agreement with one another. In springs of 1985 to 1992, the atmospheric NH_3 concentrations have been measured in Zhong Guancun District in Beijing City. The results range from 4.6 to 40 $\mu g/m^3$ with the average of 17 $\mu g/m^3$.

Key words: annular denuder, ammonia, determination of atmospheric ammonia.

The Evaluation of Economic Loss by the Acid Deposition Pollution in Chongqing. Chen Nian and Yun Qihou (Dept. of Geography, Southwest China Normal University, Chongqing 630715): *Chin. J. Environ, Sci.*, **17**(5), pp. 24—27

Acid deposition pollution in Chongqing is very serious. In order to define its economic losses, to provide a foundation for the decision making of economic and social development and to select a satisfied control plan, based on investigations in human health and damage of agriculture forest pollution, on tests of materials exposed and simulated experiment of acid deposition, using the methods of market-prices, wages costs and input-output comparison between benifits and losses, the author assessed its economic losses. The total economic losses caused by acid deposition in 1990 and 1994 are 504 million yuan and 1188 million yuan respectively, which are 2.47% and 2.0% of the GNP of the same years. The striking difference in the losses between the two years is caused mainly by the price factor.

Key words: acid deposition, economic loss, evaluation.

Fe-Si Sulfur Capture Promotion During Coal Briquet Combustion. Lin Guozhen et al. (Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085): *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 28—29

In this paper, A new Fe-Si promoter for sulfur capture was proposed for coal-briquet combustion at high temperature. Characterization of the slag left after combustion has been carried out by means of X-ray powder diffraction. A new phase $CaFe_3(SiO_4)_2OH$ was identified, which is thermally stable. This might explain its stabilizing role in sulfur fixation.

Key words: coal briquet, sulfur capture, XRPD.

COD and BOD_5 Removal Efficiencies in a Pilot Scale Constructed Reed Bed Receiving Cheese-Processing Wastewater. Huichang Zhu (Huan Qiu Environmental Engineering Co. Shanghai 201203), D.K. Stevens (Utah State University, UT84322, USA): *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 30—32

Under the influent COD concentration between 400—800 mg/L and temperature between 15—23℃, the constructed wetland functioned efficiently for COD removal. COD mass removal efficiencies reached 97 to 98%, and total removal rates reached 23.3 to 28.2 $g/m^2 \cdot d$. BOD_5 mass removal efficiencies reached 97 to 99%, while total removal rates reached 12.6 to17.2 $g/m^2 \cdot d$. The influent trench played an important role in COD and BOD_5 removal. Nearly 70 to 90% of the COD and BOD_5 removal occurred in the influent trench. During the entire experimental period, the reed bed effluent water quality met secondary discharge standards if there was no pH shock loading.

Key words: constructed wetland, subsurface flow, reed bed, control bed.

The Study on Regeneration Efficiency of Ion Exchange Resins to Enhance Nitrate Elimination. Gong Wenli et al. (Institute of Environmental Engineering Technology, Tsinghua University, Beijing 100084): *Chin. J. Environ. Sci.*, **17**(5), 1996, pp. 33—35

The enhanced nitrate elimination from groundwater by modifications of the CARIX process was described. For raw water with relative low hardness and elevated nitrate concentrations, the process was simplified by applying only an anion exchanger. In the service cycle, sulfate and nitrate species were replaced by bicarbonate species. In the regeneration step, the resin was converted into bicarbonate form by carbonic acid and magnesium oxide. Results of experiments in the laboratory scale have demonstrated that regeneration efficiency is improved apparently by adding magnesium oxide during regeneration. The optimum concentration of magnesium oxide was 0.4%. In this case, all of the resins used in the tests gained the average reduction of nitrate above 50%.

Key words: CARIX process, nitrate carbon dioxide, drinking water.