Chemical regeneration of spent powdered activated carbon used in decolorization of sodium salicylate for the pharmaceutical industry

CrossMark

Qimeng Li [a], Yanshan Qi [b], Canzhu Gao [a, *]

[a] School of Environmental Science and Engineering, Shandong University, Jinan, Shandong 250100, People's Republic of China
[b] Shandong Sanrun Environmental Protection and Technology Co. Ltd, Jinan, Shandong 250100, People's Republic of China

ABSTRACT

The purpose of this work was to regenerate spent powered activated carbon (PAC) which was exhausted in the decolorization of sodium salicylate (NaSA) liquor. In this research, a facile procedure of chemical regeneration was performed and a simple and accurate spectrophotometric method was applied. In order to obtain the optimal operation conditions, influences of following parameters were verified: soaking time, heating temperature, acid concentration and reaction time. PAC was also characterized by thermogravimetric analysis (TGA) to investigate the adsorbate–adsorbent interactions and their dependences on temperature. The optimal conditions for PAC regeneration were as follows: NaOH (1 M) soaking time of 1 h, H_2SO_4 concentration of 0.31 mol L^{-1} and agitating at 95 °C for 1 h. The peaks of derivative thermogravimetric (DTG) pyrolysis profiles of exhausted PAC appeared at low temperatures (~180 °C and ~260 °C), which demonstrated the adsorption of colored contaminants was a weak physisorption. In pilot plant experiments, it was found that after four consecutive adsorption-regeneration cycles, the adsorption capacity of PAC was maintained at high levels, even higher than virgin PAC. Therefore, this method was very simple, economical and had successfully applied in industrial scale.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Currently, activated carbon is recognized as a universal adsorbent to remove various contaminants from different matrixes (Zhang et al., 2012, 2013, 2014). Due to the advantages of high surface areas, well-developed micropores and fast adsorption kinetics, activated carbon is considered as an excellent and promising material used in gas separation (Gurrath et al., 2000), food processing (Mahapatra et al., 2012), emissions control (Lillo-Ródenas et al., 2006), catalysis (Nabais et al., 2008) and pollutant and odor removal processes (Moreno-Piraján and Giraldo, 2011). In common practice, when activated carbon reaches its saturation limit, it is simply incinerated or discarded, which gives rise to a secondary source of pollution (Dias et al., 2007; Wan and Wang, 2013). Regeneration of such material is of major importance if this process is considered economically attractive. On the other hand, the factories have been driven by increasingly stringent emission norms to regenerate and reuse saturated activated carbon (Liu et al., 2012; Ning et al., 2011; Sathishkumar et al., 2012).

Color removal is one of the most difficult requirements faced by pharmaceutical factories. Since color is a key parameter, PAC is often used to purify pharmaceuticals and their intermediates (Hernando et al., 2006). Dosage used in decoloring process is as much as 5–20 g/L of PAC/solution mixture. As a preferred adsorbent used for color removal of pharmaceuticals, the widespread utilization of PAC is restricted due to its high cost (Wei et al., 2011). Furthermore, according to the notice of Chinese Ministry of Environmental Protection for pharmaceutical industry pollution control technology (No.18 [2012]), reuse and recycle of spent activated carbon should be given priority.

Over the years, a wide variety of methods used for activated carbon regeneration have been reported. Common regeneration techniques in industrial applications are based on thermal (steam, carbon dioxide or inert atmosphere) and chemical methods (pH-swing or extraction with solvents). Being the most widely used regeneration technology, thermal regeneration will undergo sequential steps of drying, pyrolysis and gasification in a multiple hearth furnace (Alvarez et al., 2004; Maroto-Valer et al., 2006; Sheintuch and Matatov-Meytal, 1999). However, this process has some drawbacks of high cost, high-energy consumption and significant deterioration of pore structure (Ania et al., 2005a,b). Also, a considerable amount of carbon (5%–15%) is generally lost by

* Corresponding author. Tel.: +86 53188365296.
  E-mail addresses: gaocanzhuhj@163.com, liqimengzx@163.com (C. Gao).

attrition, burn-off and washout. It is also possible to heat the adsorbent electrically, but this approach would cause hot spots in the fixed bed (Ania et al., 2004). Although bio-regeneration may be considered as an economical process, the regeneration is generally slow and requires adsorbed species being totally biodegradable, which is not the case in many pollutants (Purkait et al., 2007; Yaghmaeian et al., 2014). Moreover, bio-regeneration is difficult to be industrialized. For these reasons, chemical regeneration of PAC is attractive and should be revisited. Chemical regeneration is performed through desorption or decomposition of adsorbates using specific chemical reagents (Cazetta et al., 2011). The process of chemical regeneration is performed relatively rapidly with no carbon attrition (Lu et al., 2011). Acid and alkali are traditionally used to dissolve adsorbed substances and restore the adsorption capacity. The regeneration efficiency strongly depends on the solubility of adsorbates in solvents and adsorbate–carbon surface interactions (Karanfil and Dastgheib, 2004).

The target purified product (NaSA) in the present study is a valuable intermediate chemical in the fabrication of a common acetylsalicylic acid, which is always used as a wart-removing medicine (Hernando et al., 2006). The goal of this work was to find an economic method for the regeneration of PAC which was exhausted in the decolorization of NaSA mother liquor for pharmaceutical industry. In our research, PAC pre-saturated with industrial NaSA mother liquor was regenerated with NaOH, H_2SO_4 and various redox agents by batch experiments. To this end, chemical regeneration by alkali-acid method had been successfully applied in industrial scale. Thus, this paper provides a theoretical and practical guidance for recycling waste medicinal PAC.

2. Experimental

2.1. Materials

A commercial powered activated carbon (#302) was obtained from Hangmu Timer Industrial Co., Ltd. Activated Carbon Branch, Zhejiang, China. Prior to use, PAC was washed repeatedly by distilled water to remove soluble impurities and minimize the interference of small particles. Afterwards, it was oven-dried at 105 °C for 16 h prior to storage in a desiccator. The characteristics of PAC according to the manufactor are presented in Table 1.

Sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2, 30 wt%), potassium permanganate ($KMnO_4$), ferrous sulfate ($FeSO_4$) and methylene blue (MB) were purchased from Tianjin Chemical & Reagent Co., China. All chemicals and solvents used in this study were analytical grade. All of the solutions were prepared by deionized water.

The NaSA mother liquor supplied by Xinhua Pharmaceutical Co., Ltd (Shandong, China) was selected as the test solution. The NaSA liquor contains plenty of colored impurities and pigments. All adsorption experiments were carried out with raw NaSA liquor

Table 1
Characteristics of the powdered activated carbon.

Characteristics	Specifications
Particle size (μm)	≤45
Specific surface area (m²/g)	1024
Total intrusion volume (cm³/g)	1.05
Methylene blue adsorption (mL/0.1 g)	13
Ash (%)	2.5
Acid soluble (%)	1.5
Chloride (%)	≤0.2
Heavy metal (%)	≤0.005
Moisture content (%)	≤5
pHpzc	6.6

without dilution for industrial applicability. The absorbances of fresh and treated NaSA liquor were analyzed through a UV spectrophotometer (Shimadzu, UV2450).

2.2. Adsorption procedure

According to industrial application, 0.1 g PAC is enough for 20 mL NaSA mother liquor in decoloring process. In this study, adsorption experiments were carried out with NaSA mother liquor in a temperature controlled shaker at 30 °C for 8 h, with the shaking speed of 120 rpm. When adsorptive equilibrium was reached (the equilibrium state was considered to be attained after 2 h in practical application), the solution was separated from the PAC by filtration prior to analysis. Thereafter, the absorbance of NaSA solution was determined by a UV–vis spectrophotometer. In each adsorption process, the procedure was replicated under identical conditions. Blank runs without PAC were conducted simultaneously. For each experimental point, three parallel runs were taken and only the average value was given.

2.3. Regeneration of saturated PAC

After reaching the saturation limit, spent PAC was filtered and washed with large amounts of deionized water to eliminate any excess of pollutants. Following this, the PAC was dried in an oven at 105 °C for 24 h, and then impregnated PAC was obtained. In none of the cases, and for all PAC samples assayed, did any losses of carbon mass due to careful operation.

The exhausted PAC was pretreated with 1 M NaOH solution. Firstly, adding 50 g of exhausted PAC in a 100 mL glass conical flask with 50 mL NaOH solution. Then the PAC/solution mixture was bathed and shaken in a thermal oscillator tank at 30 °C for 8 h. The resulting PAC slurry was washed with deionized water until a constant pH was reached and dried in an oven at 105 °C for 24 h to remove the moisture. The water loss rate was about 54.5% (W_{wet}: $W_{dried} = 2.22:1$). Afterwards, part of the regenerated PAC was used in adsorption procedure again, as mentioned in section 2.2. The performance of regenerated PAC was evaluated by the absorbance of NaSA solution. The lower the absorbance of NaSA solution, the more colored impurities were absorbed, which meant the regeneration efficiency was better. Note that the notation of EPAC represents the exhausted PAC which was addressed by 1 M NaOH solution.

2.3.1. Oxidation regeneration

Batch experiments were carried out with the addition of H_2O_2 in 50 mL flasks. The experiments were repeated with variations of parameters such as H_2O_2 dosage (increasing from 0.5 mL to 2.5 mL with deionized water decreasing from 9.5 mL to 7.5 mL) and temperature (75, 85 and 95 °C). Additional parameters were as follows: 5 g of dried alkali-treated PAC, 0.5 g of $FeSO_4 \cdot 7H_2O$ and 5 mL of 20 wt% H_2SO_4 solution. Afterwards, these flasks were bathed and shaken in a thermal oscillator tank for 4 h. Then, the PAC/solution mixture was filtrated by a Buchner funnel. Finally, the regenerated PAC was washed with large amounts of deionized water and oven-dried at 105 °C for 8 h.

Oxidation experiments using $KMnO_4$ as the oxidizing agent were performed in accordance with the procedure of H_2O_2 oxidation regeneration described above. Experimental parameters were as follows: 5 g of dried alkali-treated PAC, 10 mL of 20 wt% H_2SO_4 solution, 5 mL of deionized water and $KMnO_4$ with different doses (0.5 g and 1 g). Afterwards, these flasks were bathed and shaken in a thermal oscillator tank at 95 °C for 4 h. Then, the PAC/solution mixture was filtrated by a Buchner funnel. Finally, the regenerated PAC was washed with large amounts of deionized water and oven-