Water Research 114 (2017) 50–58

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Micro-milling of spent granular activated carbon for its possible reuse as an adsorbent: Remaining capacity and characteristics

Long Pan [a], Yuichi Takagi [a], Yoshihiko Matsui [b, *], Taku Matsushita [b], Nobutaka Shirasaki [b]

[a] Graduate School of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan
[b] Faculty of Engineering, Hokkaido University, N13W8, Sapporo 060-8628, Japan

ARTICLE INFO

Article history:
Received 12 December 2016
Received in revised form
9 February 2017
Accepted 12 February 2017
Available online 14 February 2017

Keywords:
2-Methylisoborneol
Iodine number
SPAC
Used carbon

ABSTRACT

We milled granular activated carbons (GACs) that had been used for 0–9 years in water treatment plants and produced carbon particles with different sizes and ages: powdered activated carbons (PAC, median diameter 12–42 μm), superfine PAC (SPAC, 0.9–3.5 μm), and submicron-sized SPAC (SSPAC, 220–290 nm). The fact that SPAC produced from 1-year-old GAC and SSPAC from 2-year-old GAC removed 2-methylisoborneol (MIB) from water with an efficiency similar to that of virgin PAC after a carbon contact time of 30 min suggests that spent GAC could be reused for water treatment after being milled. This potential for reuse was created by increasing the equilibrium adsorption capacity via reduction of the carbon particle size and improving the adsorption kinetics. During long-term (>1 year) use in GAC beds, the volume of pores in the carbon, particularly pores with widths of 0.6–0.9 nm, was greatly reduced. The equilibrium adsorption capacities of the carbon for compounds with molecular sizes in this range could therefore decrease with increasing carbon age. Among these compounds, the decreases of capacities were prominent for hydrophobic compounds, including MIB. For hydrophobic compounds, however, the equilibrium adsorption capacities could be increased with decreasing carbon particle size. The iodine number, among other indices, was best correlated with the equilibrium adsorption capacity of the MIB and would be a good index to assess the remaining MIB adsorption capacity of spent carbon. Spent GAC can possibly be reused as SPAC or SSPAC if its iodine number is $\geq$ 600 mg/g.

1. Introduction

Adsorption by granular activated carbon (GAC) is widely used in drinking water treatment to remove disinfection byproduct precursors (DBPPs), natural organic matter (NOM), and organic micropollutants (OMPs); GAC adsorption also serves as a barrier, inter alia, to occasional spikes of toxic substances in source waters (Corwin and Summers, 2012; Matsui et al., 2002b; Owen, 1998; Paune et al., 1998). Because of the limited adsorption capacity of GAC, however, removal of these compounds requires that the GAC be replaced from time to time. Otherwise, removal efficiencies deteriorate with time as the GAC filtration operation progresses. Before the breakthrough of a target adsorbate, the GAC needs to be replaced if the removal ability of the adsorbate is to be maintained. Normally, the spent GAC goes through a regeneration process because it is more cost effective to regenerate spent GAC than to purchase virgin GAC (Lambert et al., 2002; Sontheimer et al., 1988). Spent GAC is sometimes replaced with virgin GAC, for example, when the cost of virgin GAC at the market is similar to or somewhat higher than the cost of regeneration (Iwamoto et al., 2014).

In the regeneration process, adsorption sites on the GAC are refreshed by desorption, decomposition, or degradation of the adsorbates loaded on the GAC. Although regeneration restores the adsorption capacity of the GAC to an extent that depends on the regeneration process employed, there are many disadvantages to regeneration. Those disadvantages include 1) for thermal regeneration, high energy demand, loss of GAC itself, accumulation of metals in the GAC, and the high pH of water initially treated by the regenerated GAC (Lambert et al., 2002; San Miguel et al., 2001); 2) for chemical regeneration, the requirement for additional treatment to deal with the regenerants, such as organic solvents, that remain in the regenerated GAC, and the formation of by-products during regeneration (Alvarez et al., 2004; Lim and Okada, 2005; Martin and Ng, 1985); 3) for biological regeneration, the long reaction time required for regeneration and the failure of adsorption sites loaded with non-biodegradable adsorbates to recover (Nakano

* Corresponding author.
E-mail address: matsui@eng.hokudai.ac.jp (Y. Matsui).

http://dx.doi.org/10.1016/j.watres.2017.02.028
0043-1354/

et al., 2000; Scholz and Martin, 1998). There is hence a need for an alternative option to use spent GAC without regeneration.

As mentioned above, the frequency of GAC replacement is determined by the breakthrough behavior of target compounds. In water treatment plants, where multiple adsorbates are targeted for removal, the frequency of GAC replacement is determined by the earliest breakthrough of the multiple target adsorbates. Previous research has shown that NOM and DBPPs break through GAC adsorbers earlier than OMPs when these compounds coexist as mixtures in water (Kennedy et al., 2015; Summers et al., 2013). Thus, the adsorption capacities may still remain for OMPs even when the GAC has been replaced as a result of the breakthrough of NOMs and/or DBPPs.

The adsorption capacity that remains in spent GAC is likely to be low compared with the capacity of virgin and regenerated GAC. However, the disadvantage of low capacity can be compensated for if the adsorptive kinetics of the carbon is high. When spent GAC is milled into small-size particles, the increase of the exterior specific surface area leads to high adsorption kinetics that enhance the uptake rate of adsorbates. Extremely high adsorption kinetics has been reported for superfine powdered activated carbon (SPAC) with a particle diameter $\cong 1$ μm; SPAC is produced by the micro-milling of virgin powdered activated carbon (Bonvin et al., 2016; Matsui et al., 2004, 2013a).

Particle size reduction, moreover, can be expected to enhance adsorption capacities as well as adsorption kinetics (Bonvin et al., 2016; Hu et al., 2015; Knappe et al., 1999; Matsui et al., 2010). Enhancement of adsorption capacity may be mandatory for reuse of spent GAC because even very high kinetics cannot compensate for the disadvantage of inadequate capacity.

The objective of this research was to investigate the production of PAC, SPAC, and submicron-sized SPAC from spent GAC and the application of these as adsorbents to remove OMPs, in particular, 2-methylisoborneol (MIB), which is a conventional target OMP due to its association with an unpleasant earthy/musty taste and odor, which impair the palatability of drinking water (Cook et al., 2001; Newcombe et al., 1997). Changes of equilibrium adsorption capacities and adsorptive removal rates with carbon particle size and carbon age are discussed in conjunction with the metrics of standard indicators of activated carbon characteristics.

2. Materials and methods

2.1. Activated carbon

GACs were collected from GAC beds of drinking water treatment plants operated by the Bureau of Waterworks of the Tokyo Metropolitan Government, the Public Enterprise Bureau of Ibaraki Prefectural Government, and the Ishikari-Seibu Water Supply Authority (Table 1). After being thoroughly mixed, each GAC was separated into several portions and kept under a moist condition at 4 °C in a refrigerator. Some portions were sterilized by autoclaving or gamma ray irradiation, which are described in detail in Section S1 of the Supplementary Information (SI). Unless specified, the sterilized samples discussed in this paper refer to the samples autoclaved at 63 °C for 30 min.

The GACs were pulverized into fine particles of three particle-size categories according to their median diameter (D50): powdered activated carbon (PAC, D50: 12–42 μm), superfine PAC (SPAC, D50: 0.9–3.5 μm), and submicron-sized SPAC (SSPAC, D50: 0.22–0.29 μm). The GACs had D50s of 1.5–2.3 mm. The details of the pulverization process and the particle size distributions of all carbon samples are described in the SI (Section S2 and Fig. S6). Tables S1–S3 of the SI list all activated carbon samples and related experimental applications. These samples were given unique three-term designations as follows. The first term indicates the name of the water treatment plant where the GAC was collected and the number of years the GAC was used (note: zero "0" year indicates virgin carbon). The second term indicates the method of pretreatment of the GAC. An "n" indicates "no pretreatment", "a" indicates "autoclave pretreatment", and "g" indicates "gamma irradiation pretreatment". The final term indicates the particle size category of the carbon: GAC, PAC, SPAC, and SSPAC. KM2-a-SPAC, for example, means SPAC produced by milling from autoclaved GAC, which was sampled at the Kanamachi Water Treatment Plant after being used for 2 years. The carbons produced from the GACs given no pretreatment were used for adsorption experiments with carbon-water contact times < one day. Those produced from the GACs pretreated by autoclaving were used for adsorption experiments with carbon-water contact times > one day to avoid any biodegradation effect. Autoclaving did not substantially influence the equilibrium adsorption capacity (e.g. sections S1.2 and S1.3 of the SI). The PAC, SPAC, and SSPAC samples were stored in ultrapure water in the form of slurries at 4 °C after vacuum conditioning for 20 min to remove any air from the activated carbon pores.

The pore size distributions of the activated carbons were obtained by using the nitrogen gas adsorption-desorption method (Autosorb-iQ, Quantachrome Instruments, Kanagawa, Japan). The isotherm data for nitrogen gas at 77.4 K was analyzed by (1) the Barrett-Joyner-Halenda (BJH) method for the mesopore region (pore width >2 nm) and (2) the quench solid density functional theory (QSDFT) for the micropore region (pore width = 0.6–2 nm) (ASiQwin, ver.3.01, Quantachrome Instruments). Iodine, phenol, methylene blue (MB), and sodium liner-dodecylbenzene sulfonates (hereafter ABS) numbers were measured according to the standard methods of the Japan Water Works Association (K 113:2005-2) (JWWA, 2005). The details of the measurement methods are described in Section S3 of the SI.

2.2. Adsorbates

MIB was the main target compound in this study. Reagent MIB was dissolved in natural water (the raw water entering the Kanamachi Water Purification Plant, the same plant where the main target GACs were collected) or in organic-free ionic water that was made from ultrapure water by adding ions at concentrations identical to their concentrations in the natural water (details are provided in Section S4 of the SI). The concentrations of MIB were measured by using deuterium-labeled geosmin (geosmin-d3) as an internal standard in a purge-and-trap concentrator (P&T) coupled to a gas chromatograph-mass spectrometer (GC/MS); the *m/z* 95 peak was assumed to correspond to MIB and the *m/z* 115 peak to geosmin-d3. Two P&T-GC/MS systems were used: (1) a Model 4660 Eclipse (Kinryo Electric Co., LTD, Osaka, Japan) coupled with an Agilent 7890A/5975MSD (Agilent Technologies, Inc., CA, USA); and (2) an Aqua PT 5000 J (GL Sciences, Inc., Tokyo, Japan) coupled with a GCMS-QP2010 Plus (Shimadzu Co., Kyoto, Japan).

In addition to MIB, some compounds with environmental relevancy and compounds used for adsorbability indices were tested as supplementary adsorbates: geosmin, iodine, phenol, acetaminophen, MB, ABS, poly(styrenesulfonic acid) sodium salt with an average molecular weight (MW) of 210 (PSS-210), and PSS-6400 with average MW 6400. These compounds were selected to cover a variety of hydrophobicities and molecular sizes. Section S5 of the SI provides details of the anaytical methods used to quantify these compounds. Except for PSS-210 and PSS-6400, which were purchased from Sigma-Aldrich Co. LLC. (St. Louis, Missouri, USA), all of these chemical reagents were purchased from Wako Pure Chemical Industries, Ltd., (Osaka, Japan).