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Characteristics of adsorptive removal of 2-methylisoborneol by micro-milled activated carbon
(超微粉碎活性炭による 2-メチルイソボルネオールの吸着除去特性)

In both research and practice of water purification technology, superfine powdered activated carbon (SPAC), which is produced from conventionally sized powdered activated carbon (PAC) by wet milling in a bead mill, has attracted attention for its higher adsorption capacity of contaminants as well as the higher adsorptive uptake speed than its parent PAC. However, the previous SPAC researches only focused on the SPAC with a median diameter (D50) around one to a few micrometers which were produced from fresh PAC by wet milling system. With the improvement of milling technology, 1) the similar sized SPAC can also be produced by dry milling, and 2) the submicron SPAC with D50 less than 200 nm (termed as SSPAC, submicron-sized SPAC) can be produced by wet milling. Considering that few researches touched the above two points, this doctoral work attempted to fill in the blanks by investigating the adsorption performance of dry-milled SPAC and also the wet-milled SSPAC, in particular, comparison with the wet-milled SPAC. What's more, much effort was put into applying the wet-milling technology to the reuse of spent activated carbon.

To evaluate the adsorption performance of activated carbons, 2-Methylisoborneol (MIB), an earthy-musty compound commonly targeted by activated carbon adsorption in water treatment systems, was chosen as the main target adsorbate together with some other supplementary adsorbates. According to the results of experiments, some findings were concluded.

1) Dry-milled SPAC exhibited lower adsorptive removal of MIB than wet-milled SPAC, even when both SPACs were produced from the same PAC and were composed of particles of the same size. One reason for the lower removal of MIB by the dry-milled SPAC was a higher degree of aggregation in the dry-milled SPAC after production; as a result, the apparent particle size of dry-milled SPAC was larger than that of wet-milled SPAC. The dry-milled SPAC was also more negatively charged than the wet-milled SPAC, and, owing to its higher repulsion, it was more amenable to dispersion by ultrasonication. However, even after the dry-milled SPAC was ultrasonicated so that its apparent particle size was similar to or less than that of the wet-milled SPAC, the dry-milled SPAC was still inferior in adsorptive removal to the wet-milled SPAC. Therefore, another reason for the lower adsorptive removal of dry-milled SPAC was its lower equilibrium adsorption capacity due to the oxidation during the milling. The adsorption kinetics by SPACs with different degrees of particle aggregation were successfully simulated by a pore diffusion model and a fractal aggregation model.

2) It has been known that adsorption capacity increases or un-changes with decreasing carbon particle size and SPAC have similar or higher capacity than PAC. In the smaller particle size range (1.5 μm to 150 nm), however, this study revealed that the adsorption capacity was lowered with decreasing carbon particle size for MIB and some other low-molecular-weight (LMW) compounds. The phe-

nomenon was related to the oxidization of the carbon during the intensive milling to reduce particle size to around 150 nm. The oxidation would modify the chemical property, in particular, the hydrophobicity, of carbon, thus reducing adsorptive affinity to hydrophobic compounds, such as MIB. This study was also successful to control carbon oxidation during the milling. The MIB adsorption capacity on SSPACs of low oxygen contents was higher than on those of high contents. Finally, this study revealed that the carbon particle size reduction by milling would enhance the adsorption capacity, but over-milling reduce the capacity rather than increase.

3) A variety of granular activated carbons (GAC), which had used for 0 to 9 years in water treatment plants, were collected and milled to carbon particles of different sizes of different ages. SPAC produced from 1-year old GAC and SSPAC from 2-year old GAC showed a similar ability of MIB removal to virgin PAC in the carbon contact time of 30 minutes, which suggested the potential reuse GAC by milling. The potential was due to the increase of equilibrium adsorption capacities by the reduction of carbon particle size as well as improved adsorption kinetics. During the long-term (>1 year) use in GAC bed, pores, in particular for pores with the width of 0.6 to 0.9 nm, in the carbon was significantly reduced. Therefore, the equilibrium adsorption capacities of the compounds having the molecular size of this range could be decreased with increasing the carbon age. Among these compounds, the capacity decrease was prominent for hydrophobic compounds including MIB. For the hydrophobic compounds, however, the equilibrium adsorption capacities increased with the reduction of carbon particle size. Iodine number among other indices was the best correlated to the equilibrium adsorption capacity of MIB, and it would be a useful index to access the remaining MIB adsorption capacity in spent carbon. Spent GAC can be reused as SPAC or SSPAC if it has the iodine number of around 600 mg/g or more.

Overall, this research clarified the merits and demerits of micro-milling to produce SPAC and SSPAC in terms of MIB removal. Merits are higher adsorption capacity as well as higher adsorption kinetics on SSPAC and SPAC than on PAC. Because of this merit, spent GAC could be reusable: SSPAC from 2-years old GAC and SPAC from 1-year old GAC exhibited the same MIB removal performance as virgin PAC. Demerits are oxidation and aggregation, which were observed for virgin carbons. SPAC produced by dry-milling showed the aggregation of particles and the increase of oxygen content indicating the decrease of hydrophobicity. SSPAC was much smaller in particle size than SPAC but has a higher content of oxygen. Because of these reasons, dry-milled SPAC and wet-milled SSPAC were not superior to wet-milled SPAC.