Advice & Counsel

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That Lump of Coal - Part 3

Dear Advice & Counsel,
My company has asked me to look into recycling our treated wastewater back to our plating lines. While I think I have a handle on the basics, like TDS reduction using ion exchange, I'm not sure I know enough about organics removal using carbon. Can you shed some light on this topic?

Signed,
Fusili Carbonera

In June and July, I offered this series on carbon treatment of wastewater. Continuing our discussion:

Source and activation of carbon

What makes AC an effective media for adsorption of organic compounds is its structure (highly porous and a vast amount of surface area) and the fact that in the activation process, all bonds between carbon and organics that may reside on the surface are destroyed, leaving the exterior carbon atoms in an "active" state. The raw material used to produce activated carbon can have a pronounced effect on the surface area, pore sizes, pore distribution, hardness and surface area and will therefore affect its performance. Raw materials include coal (bituminous and lignite), wood, gas, peat, petroleum residuals, coconut/nut shells and several other natural materials including seeds from various fruit. The most common source of carbon for wastewater treatment systems is lignite/bituminous coal and wood.

Although numerous physical forms of carbon are commercially available for wastewater treatment, activated carbon is sold in two basic forms: powder (PAC) and granular (GAC). PAC is generally limited to batch carbon treatment systems, while commercially available continuous treatment and filtration systems most often employ granular carbon.

Activation involves the following steps:

1. The raw material is pulverized/crushed to modify physical characteristics such as hardness.

2. In the presence of an oxidizing gas (but an absence of oxygen), the raw material is thermally treated at three different temperatures to burn off surface organics and create porosity. The first temperature (~170°C) removes all moisture. This is followed by another thermal treatment at about 280°C. During this step, a significant amount of the carbon is lost as monoxide and dioxide gases and pores are created where the carbon is lost. A final burn at about 600°C completes the burn and assures that any organics that may have been bonded to the surface of the carbon have been "carbonized." About 20 to 25% of the starting material is lost in this burn off step.

3. The second step employs carbon dioxide or steam at about 900°C, causing the destruction of any remaining decomposition residues from Step 1. This process also expands the existing pores and produces additional porosity in the carbon yielding an extremely high surface area. Keys to successful activation include:

   - The type/concentration of the oxidizing gas employed
   - Reaction time
   - Reaction temperature
   - Source material

4. After activation, the carbon may be further processes by crushing, sieving, grinding, acid treatment and rinsing prior to drying/packaging.

Chemical activation

An alternate activation process involves soaking the source material with phosphoric acid, caustic soda or zinc chloride and then carbonizing it for a controlled amount of time at temperatures ranging from 450 to 900°C. Under these conditions, conversion to carbon and activation occur simultaneously. Activated carbon produced in this manner can be produced more quickly and possibly at lower temperatures and it may be less expensive, but it may also contain chemical residuals that can affect performance.

Choosing a carbon

In choosing a carbon to be used for treating wastewater, we need to consider a number of characteristics that will affect the quality/suitability of the carbon to a specific task.

Virgin versus regenerated carbon

Because most applications in metal finishing are too small in scope to justify regeneration systems, virgin carbon is most commonly employed. However, since carbon may be commercially regenerated, it is a good idea to confirm whether virgin or regenerated carbon is being supplied, as regenerated carbon typically offers a lower level of performance.

Surface area

The surface area of AC is typically given in m^2/gram or m^2/pound. One pound of carbon may contain a surface area as large as 500,000 m^2 (125 acres). The total surface area of a given carbon sample is measured by its adsorption of nitrogen gas. Because nitrogen gas molecules are small relative to the organic molecules adsorbed by the carbon, this "measured" surface area can be misleading. Depending mainly on the source and activation methods employed, the surface area may range from 500 to 1400 m^2/g, with areas as high as 2500 m^2/g reported in the literature.

Higher surface area is not always better. According to Perrich, adsorption isotherm studies have shown that lower surface area carbon can outperform higher surface area carbon when the organics have a molecular weight range of 350 to 1370.

The surface area of a given sample of carbon is not a reliable predictor of adsorption performance because adsorption performance is affected by that portion of the surface area that is wetted by liquid, not the total surface area. Also, some organics may be too large to travel through micropores (which provide the bulk of the surface area) and can not be adsorbed.

Carbon density

The density of carbon is typically given in kg/m^3, kg/L, g/mL or lb/ft^3. Higher densities tend to provide lower levels of losses during handling due to abrasion. The amount (weight) of carbon held in a given vessel is determined by its density. In filtration systems, more flow can be treated (before regeneration or replacement of the carbon), if high density carbon is employed as opposed to low density. In batch treatment systems, the more dense powdered carbon settles faster and produces a more dense solids layer at the bottom of the treatment tank.

Particle size, distribution and shape

Finer AC particle sizes provide faster access to the adsorption sites and therefore improve adsorption kinetics. The particle size affects the adsorption rate, usable flow rate and backwash rate of a carbon adsorption system. Particle size is typically given in "mesh" sizes of U.S. standard sieves. Based on which mesh screen retains more than 90% of the material, the carbon is given a size (*e.g.*, 8 × 16, 20 × 40). GAC particle size may range from 0.5 to 1.7 mm, and is normally > 20 mesh/0.8 mm. PAC has a particle size < 0.15mm (100 mesh). The uniformity of the carbon particles is also important. Perrich recommends a uniformity coefficient of 2.1 or less.

The shape of the carbon particle is a product of the raw material employed and the handling and sieving processes employed at the manufacturing facility. The shape of carbon has a large impact on operating pressure in both downflow and upflow adsorption equipment. High operating pressure requires more sophisticated (expensive) equipment.

Pore size, range and volume

The majority of most any carbon sample's surface area is made up of channels and pores. The pores may be "micropores" (< 2 nm) or "macropores (> 50 nm) and "mesopores" (2 to 50 nm). Most of the adsorption of organics takes place on the surface of micropores. The others can be thought of as "channels" to the micropores. In general, GAC from petroleum (coke) products tend to have smaller, while carbon from lignite coal tends to have the largest pore sizes and range. GAC from bituminous coal falls in between coke and lignite. In general, GAC has larger internal surface area and smaller internal pores. PAC has larger pores and a smaller internal surface area. Carbon products for wastewater applications tend to have a significant percentage of pores in the 20 to 500 Å range, providing effective contact between water and carbon.

The pore volume is an indication of the space within the carbon particle occupied by holes. The pore volume and surface area distributions, which can vary between carbon products, can affect adsorption rate and efficiency.

Adsorption capacity

Adsorptive capacity has a big impact on capital and operating cost for carbon treatment. Adsorptive capacity provides information on the performance of a given carbon in removing organics based on molecular weight. Adsorptive capacity is given by a series of "numbers" which indicate the performance on different molecular sizes of organics:

The "iodine number" (mg iodine/gram carbon) is a measure of the adsorption capacity of low molecular weight organics for a given carbon sample. A higher iodine number indicates a higher ratio of small pores in the carbon (< 20 Å)

The "methylene blue" number is a measure of the ability of a given carbon to adsorb medium sized (those adsorbed in 20 to 500 Å pores) organic molecules. MB numbers are in the 0.011 to 0.028 g/g range.

The "molasses number" (mg molasses/gram carbon) is a measure of the adsorption capacity of high molecular weight organic molecules. A higher molasses number indicates a higher ratio of large pores in the carbon (20 to 500 Å). In comparing carbons, if two samples have essentially the same pore volume, the one with the higher molasses number will tend to yield higher adsorption capacity and faster adsorption rates. Molasses efficiency is related to molasses number (600 = 185%, 425 = 85%). The European molasses numbers (range 525 to 110) are the inverse of those reported in the U.S.A.

The "phenol number" (mg phenol removed/gram of carbon) is indicative of the ability of the carbon to remove taste, odor and color from wastewater.

Abrasion number (hardness)

Carbon may be transported by pumping a slurry. It may also be handled by conveyors, and it will tend to "rub" against itself as it travels down a column, during backwash and in the handling involved in regeneration systems. Resistance to abrasion (hardness) is therefore a measure of the stability of the granule under such conditions. The abrasion number measures the ability of carbon to resist breakdown to smaller particles. The abrasion number (a.k.a., hardness number) is typically the percent reduction in average particle size under specific test conditions. Harder carbon will hold its shape better and reduce virgin carbon consumption. The level of hardness of a given carbon is mostly related to the raw material used in its manufacture. Carbon with higher abrasion numbers have lower operational costs. Granular carbons having abrasion numbers of less than 25 are typically employed in carbon treatment systems for wastewater.

Ash content

Higher quality AC will have lower ash content. The amount of ash left after a given sample of AC is completely destroyed thermally, is a function of raw materials used and manufacturing methods employed. If regeneration systems are used, the ash content is also a product of the regeneration process.

Ash reduces the adsorption capacity of the carbon and can impact regeneration as well. Elements commonly found in ash from AC include iron, silica, calcium and aluminum. While these tend to resist leaching, if any do leach from the carbon, they can contaminate the treated water, render it turbid or yield undesirable color.

The above comparison criteria are just the beginning of the selection process. Other properties that may need to be considered are moisture and ash content. Once a choice is made from competitive products, bench testing of the top two/three choices needs to be conducted to confirm suitability and performance.

We will continue this series of articles next month. ***P&SF***