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That Lump of Coal - Part 2

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

Last month, I began answering "Ms. Carbonera's" question on carbon treatment of wastewater. Continuing our discussion:

How carbon works

Activated carbon is non-polar and has an extremely large surface area and porosity level. This allows it to overcome the forces that keep a non-polar dissolved organic dissolved in water, which we learned in our chemistry lesson is a polar molecule. The force holding the organic molecule on the surface of the carbon is called a "van der Waals" force. Van der Waals forces can be thought of as temporary (weak) attractions between the organic molecules and the carbon, caused by unevenly distributed electrons in the molecules.

Due to differences in the activities of organic compounds versus the activated carbon, adsorption proceeds in four steps:

1. The organic molecule diffuses/travels through the bulk solution to a thin layer of liquid between the bulk liquid and the activated carbon surface. In this layer, there is a significant difference between the bulk water organic concentration (much higher) and the diffusion layer organic concentration (much lower). This process is slow and may be the key adsorption rate determining step. Turbulent flow and agitation levels minimize the time for this process step.
2. The organic compound diffuses through this thin layer of liquid between the particle surface and the liquid, down to the surface of the carbon. The thickness of the boundary layer of water is also dependent on the level of agitation, so this step may combine with the first step to yield the overall adsorption rate value.
3. The organic molecule is adsorbed into a pore. This step is relatively quick.
4. Depending on the molecule/pore size(s), the organic is held in place by van der Waals force(s) at various pore depths. This step is also relatively fast.

Predicting the performance of any candidate carbon sample based on kinetics and carbon properties for any specific application is very difficult, if not nearly impossible. Perrich's model for the adsorption process divides it into four separate rate controlling steps of decreasing adsorption rates:

1. Initially the adsorption rate is controlled by the transfer rate across the diffusion layer of the external surface of the carbon, until these sites are exhausted.

The next three successive rate controlling steps are:

2. Adsorption on macropores (5000 to 20,000 Å)
3. Adsorption on medium-sized pores (20 to 100 Å)
4. Adsorption on micropores (10 to 20 Å)

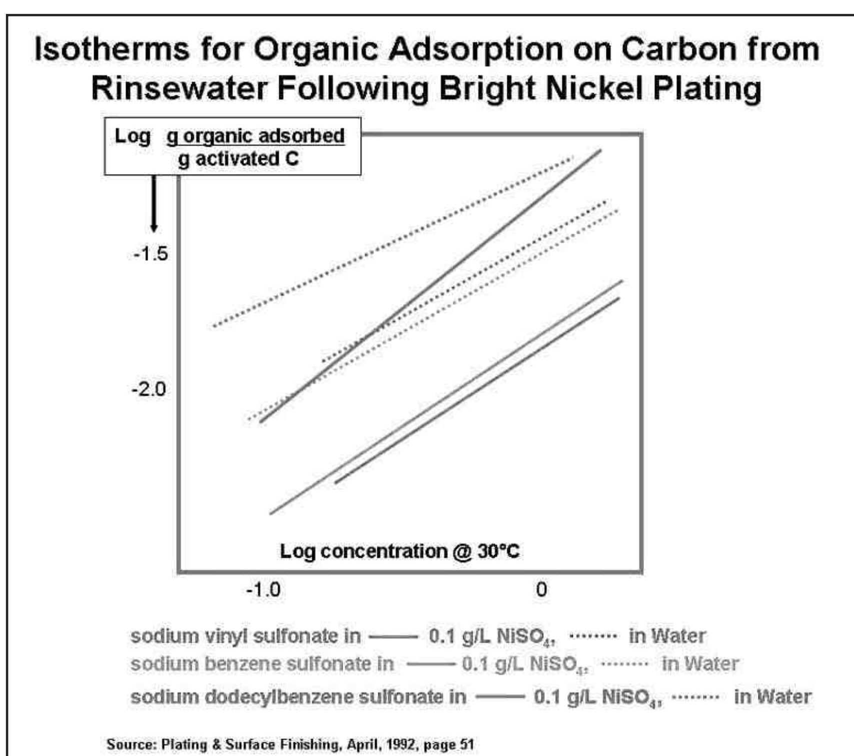

Figure 1.

Adsorption kinetic data based on this model can be plotted as "isotherms" (a.k.a., Freundlich isotherms). Figure 1 is a set of isotherms developed by Huang (*Plating & Surface Finishing*, **77** (4), 50, 1992) for the adsorption of organics one might find in rinsewater following bright nickel plating.

An isotherm is a plot of removal of an organic per unit weight of carbon as a function of the concentration of the impurity remaining in the solution under equilibrium conditions. Isotherm plots can be used to evaluate carbon treatment efficacy and predict residual organic concentration for wastewaters that are contaminated with one major organic or for wastewater containing a mix of organic compounds that are low in concentration. An isotherm is specific to a particular contaminant and the type of activated carbon used. Therefore the Freundlich isotherm may not be an accurate predictor when the wastewater contains a high concentration of organics, a wide assortment of organics or organics that are less amenable to sorption than those tested for.

General adsorption tendencies of organics

Solubility

In general, polar (soluble) organic molecules exhibit a low level of adsorption on carbon as their attraction to water acts as an opposing force. Organic molecules that exhibit a low level of solubility tend to be more readily adsorbed onto carbon.

Ionization

Compounds that are strongly ionized in water are generally not adsorbed with the possible exception of hydrogen ions at relatively high concentration (highly acidic) conditions.

pH

The optimum pH in any specific application for treatment of wastewater must be determined by bench scale testing. For example, a low pH may enhance the adsorption of organic acids. A high pH may increase the adsorption rate of organics that are alkaline in nature. Phenol and phenolic salts are best carbon treated at neutral or low pH.

Carbon/water temperature

Under the temperature conditions normally encountered in wastewater treatment systems, the adsorption tendency is not significantly affected. However, temperatures below 60°F may enhance adsorption while those above about 100°F can adversely affect adsorption.

Mix of organics

The blend of organics present in raw wastewater can hurt, help or have no effect on adsorption of same. Which one happens depends on the types of molecules, molecular sizes, adsorption affinities and concentration of each compound present. Since this is the most common condition of metal finishing wastewater and because this condition prevents accurate prediction of adsorption rates and mass loadings, bench scale testing to produce isotherms is necessary when designing most any carbon treatment system for metal finishing wastewater.

The level of adsorption (rate, magnitude) in a specific application will depend on a number of factors:

Molecular structure of the organic

The polarity and or solubility of an organic will affect its tendency to adsorb onto AC. Branched-chain aliphatics are favored over non-branched straight-chain compounds. The nature of any functional groups will also affect adsorption. For example, hydroxyl and amino groups tend to reduce the level of adsorption, while the presence of aromatic rings and nitro groups increases this tendency.

Non-polar and low-polar organics are favored over polar molecules. Molecules of low solubility are more effectively adsorbed than those that are highly soluble (example primary alcohol, ~4% vs. benzene, ~95%).

Larger molecules (up to a limit) tend to have more adsorption sites and are therefore favored over small molecules as long as the molecules are not too large for the smallest pores in the carbon.

Inorganic compounds vary in level of adsorption ranging from non-adsorbable ions such as those from dissociated salts (sodium, potassium, chloride, sulfate) to ferric and mercuric ions which can be adsorbed to some extent to precious metals ions such as gold, platinum, silver and palladium which are strongly adsorbed. As an example, carbon treatment of some gold plating solutions can adsorb as much as 1 troy ounce of gold per 10" carbon filtration cartridge. Carbon can also remove some anions such as nitrates and chlorides.

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

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