Advice & Counsel

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That Lump of Coal

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

Dear Ms. Carbonera,
You might want to get a hold of a textbook titled *Activated Carbon Adsorption for Wastewater Treatment*, by Perrich for an exhaustive treatise on the subject. However, I will attempt to distill the subject to a few magazine pages for quick reading.

Carbon (usually as peat or coal) is readily found in nature. Carbon has three commonly found allotropic forms: amorphous, graphite and diamond. A fourth uncommon form of carbon is buckminsterfullerene, C_{60}, which has recently been produced by the treatment of graphite with lasers. Carbon displays unusual chemical and physical properties. Despite the presence of two unpaired electrons in the outer shell (which typically makes an element reactive in nature), carbon is relatively inert in most electrochemical reactions and in fact, is often used as an insoluble anode in electroplating baths. An example of such use is a commercially available trivalent chromium plating solution. The fact that carbon is inert allows us to use it to remove undesirable organic impurities from some plating solutions without altering the remaining solution chemistry.

Carbon displays a wide range of hardness values. Graphite, for example, is very soft while a diamond is one of the hardest substances found in nature. Carbon can be found as carbon dioxide in the air and dissolved carbon dioxide in water and carbonated beverages. It can be found in stones (calcium carbonate) and in coal, petroleum oil and natural gas. Graphite can be changed to a diamond structure under high temperature and pressure (>125 K-bar) conditions, when a catalyst such as platinum, iron or chromium is employed. If the temperature is high enough for the catalyst to melt, graphite dissolves into the metal while diamond precipitates out.

In metal finishing, numerous operations contain ingredients and or additives that are "organic" compounds. A basic definition of an organic compound is: "any chemical compound that contains the element carbon." Examples of such compounds used in metal finishing include complexing agents and surfactants in cleaners and plating solutions (examples: EDTA, sodium lauryl sulfonate), most all plating solution brighteners (example: saccharin), plating solution leveling agents (example in nickel plating: coumarin, pyridine), acid inhibitors (example: butyne diol), passivation solutions for stain prevention of copper and silver (example: mercapto benzo triazol) and even in wastewater treatment (example: floccing agents). The total number of organic compounds used by the simplest metal finishing facility can easily exceed 100.

A typical wastewater treatment system does not remove or destroy organics, and often adds to the organic loading instead. If the treated wastewater is routed to a sewer, the organics in the wastewater are typically not regulated by USEPA (but may be regulated on a local level). If the treated wastewater is routed to surface water (river), the organic content is typically regulated under NPDES permit requirements and is monitored using analytical tests such as TOC (Total Organic Carbon), COD (Chemical Oxygen Demand) and BOD (Biological Oxygen Demand). Depending on the operations employed, wastewater may also contain undesirable color and or odors, which can be treated with carbon.

The presence of a high concentration of organic compounds along with the presence of dissolved inorganic ions in the treated wastewater makes recycle/reuse of the treated wastewater impractical for most metal finishing operations, except those that require minimal rinse purity, such as after aqueous cleaning. Therefore, for compliance purposes and to allow for recycle of treated wastewater without contaminating the process solutions, a method of organic removal needs to be employed.

Carbon treatment with activated carbon (AC) removes organics from treated wastewater through the process of adsorption (Some scientists argue it's more absorption than adsorption, but we will not enter into that argument and go with the conventional thinking). Use of AC is relatively inexpensive and the process can remove a broad range of organic compounds without requiring major changes in water chemistry. In some cases, an organic contaminant may be selectively removed by adjusting the type of carbon employed and the condition of the water (temperature, pH).

According to Calgon Carbon Corporation, over 80% of the European Union List I and II toxic substances under the Dangerous Substance Discharges Directive of 1976 (76/464/EEC) and 1986 (86/280/EEC) are well adsorbed by activated carbon.

Water containing organic compounds looks no different than water containing none (unless the organics are part of an emulsion). There are analytical methods for detecting said organics. Those most commonly employed are briefly described here.

TOC (total organic carbon)

Since organic compounds are those that contain the element carbon, we can obtain a measure of the level of organic contamination by testing the water for carbon from organic compounds. A typical analysis for TOC measures both the total carbon present as well as the inorganic carbon. Subtracting the inorganic carbon from the total carbon yields TOC.

The more common method for analyzing TOC uses an acidified (pH <2) sample of the wastewater, releasing any inorganic carbon as CO_2 gas. The remaining non-purgeable CO_2 gas contained in the sample is then oxidized within the analytical instrument, releasing more CO_2, which is routed to a detector for measurement.

As an example, the rinsewater from a bright nickel plating tank may contain 4,000 ppm TOC. After carbon treatment, the TOC in the rinsewater may be less than 50 ppm.

"Activating" Carbon

The term "activated carbon" refers to carbon materials, such as coal or wood that are processed through dehydration, carbonization and oxidation to yield a material that is highly adsorbent due to a large surface area and high number of internal pores per unit mass. As wastewater flows through a bed of carbon materials, molecules that are dissolved in the water tend to become trapped in these pores.

In general, organic constituents with certain chemical structures (such as aromatic functional groups), high molecular weights and low water solubilities are amenable to activated carbon adsorption. Eventually, as the pore spaces in the carbon become filled, the carbon becomes "spent" and ceases to adsorb contaminants. Spent carbon may be regenerated or disposed of.

Spent carbon can be regenerated using steam, thermal or physical/chemical methods. For most metal finishers, regeneration can not be economically justified, and the spent carbon is disposed of as a special or hazardous (depending upon characteristics) waste and is replaced. An alternative to disposal or on-site regenerations is to ship the spent carbon back to a commercial treatment-regeneration facility (the number of vendors offering this service is small). While regeneration is not typically conducted by metal finishing facilities, larger users such as POTWs (Publicly Owned Treatment Works) and TSDs (Treatment Storage & Disposal facilities) may utilize regeneration to reduce operating expenses . Thermal and steam regeneration are the most common methods employed by such facilities. These methods volatilize the organic compounds that have adsorbed onto the carbon. In many locations thermal oxidation is necessary to meet local and state air pollution control regulations. A scrubber may also be necessary to remove particulates. Regeneration reduces solid waste handling problems and can save up to 50% of the carbon cost.

Carbon adsorption depends on process conditions such as temperature and pH and a number of process design parameters including carbon/wastewater contact time, carbon adsorption capacity, the nature of the carbon employed and the type of equipment employed. Carbon adsorption capacity also depends on the equipment and the nature of the adsorbed compounds.

Advantages of carbon adsorption

Activated carbon is relatively inexpensive and offers an extremely high internal surface area provided by an intricate network of internal pores. The structure can be envisioned as "Swiss cheese"-like. Carbon adsorption is a highly effective, well proven technology for removing organics from water, wastewater and chemical processing solutions (example: nickel and acid copper plating solutions). Carbon removes a broad range of organics, including dyes and compounds producing undesirable coloration and odor in water. Adsorption of organics generally increases with increasing molecular weight and decreasing solubility of the organics to be removed. Carbon treatment can reduce organics down to the ppb level under properly controlled circumstances.

Since continuous carbon treatment systems typically involve simple pumping systems, they are easy to start up and shut down as required. Carbon treatment systems may be small enough to be portable. Space requirements are low. Carbon adsorption can be easily incorporated or added on to an existing wastewater treatment system.

Limitations of carbon adsorption

Activated carbon does not bind well to primary alcohols, glycols, ammonia, strong and some weak (example: boric) acids, basic molecules, non-precious metals, sodium potassium, fluorides and a host of additional elements and compounds.

It takes a large volume of carbon with a large surface area to remove any significant quantity of organics from an aqueous solution. The total surface area of activated carbon has been reported to be between 450 to 1800 m^2/g with pore volumes of 0.7 to 1.8 m^3/g. However, the adsorption efficiency for any specific organic or family of organics is dependent, in part, on the pore size and pore size range of a given sample of carbon. Therefore, the total surface area and pore volume are not necessarily the best parameters in choosing the right carbon for a given task. As an example, AC with a high a total surface area as (> $1000 m^2/g$) and low pore volume (< 0.6 m^3/g) may be effective in adsorbing organics from gaseous flows, but is ineffective at adsorbing those same organics from a flow of water.

Conditions which tend to favor adsorption include:

pH

In general, lower pH values favor organic adsorption, while higher ones hinder adsorption.

Temperature

Because higher temperatures tend to lower viscosity and increase energy, adsorption rates tend to be higher at elevated temperatures.

Pore size

Activated carbon with more of the pore population in the larger sizes tends to adsorb preferentially organics with higher molecular weights (and visa versa).

The correct carbon source

For any given task or set of tasks, bench testing to determine the right carbon and identify operational variables is highly recommended.

More next month

Further Reading and Contacts:

J.P. Pope, "Activated Carbon and Some Applications for the Remediation of Soil and Groundwater Pollution," Virginia Tech Internet Publication, Blacksburg, VA, 1999, http://www.cee.vt.edu/ewr/environmental/teach/gwprimer/group23/webpage.htm

W.F. Naylor, & D.O. Rester, "Determining Activated Carbon Performance," *Pollution Engineering* (July 1, 1995).

J.R. Perrich. *Activated Carbon Adsorption for Wastewater Treatment*, CRC Press, Boca Raton, FL, 1981.

R. Roll & D. Crocker, "Evolution Of A Large Activated Carbon Secondary Treatment System," *Proc. WEFTEC 1996, WEF Annual Conference, Dallas, TX*, Water Environment Federation, Alexandria, VA, 1996.

G. Tchobanoglous & F.L. Burton, *Wastewater Engineering: Treatment and Reuse*, 3rd Ed., Metcalf and Eddy Inc., Wakefield, MA, 1991.

U.S. EPA, *Granular Activated Carbon Systems: Problems and Remedies*, U.S. EPA No. 832-R-84-104, U.S. EPA, Washington, DC, 1984.

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Jeff Cannis to serve as new Technical Services and Facilities Manager at Technic

Jeff Cannis has joined Technic (Anaheim, CA) as Manager, Technical Services. Jeff will have responsibility for the technical service function in support of Technic's Western Region customers. Jeff will also oversee the analytical laboratory, wafer plating lab and certain facilities management functions. Having previously held key roles in senior management for Amkor, Delphi Jade Technologies and TRW Cinch Connector, Jeff brings extensive processing engineering, lab management and a technical electroplating background to Technic. Jeff holds a B.A. degree in Chemistry and has a strong technical background in semiconductor packaging.

Notes John Garrigan, Technic's Corporate Account Business Manager, "The markets we serve are increasingly competitive. Technic has differentiated itself in the marketplace by obtaining the best people with the kind of technical background and customer service dedication that sets us apart from our competition. Jeff is a welcome addition to the Technic team and we look forward to his leadership in further expanding our customer service and technical support."

Coventya, Inc. adds key personnel

Coventya, Inc. is pleased to announce the addition of **Brad Durkin**, joining as the Vice President of Strategic Business Development to the Coventya family. Brad will be located at the Coventya Technology Center in Cleveland, Ohio.

In addition to a Bachelor of Science Degree in Chemistry, Brad has over 25 years of broad experience in the metal finishing industry, with 21 years accumulated at Allied Kelite/MacDermid, with positions ranging from technical service to technology and business management. In his last eight years at MacDermid, he served as Global Director for the Engineering Technologies Business Group, responsible for managing the marketing, R&D, technology acquisitions and training activities for various company strategic technology platforms. Prior to joining Coventya, he spent 18 months at the Whyco Finishing Group working as their Corporate Director of Marketing and Technology Development.

Brad continues to participate in various industry groups including NASF, ASTM, SAE, NACE and the EN steering committee, where he enjoys presenting to customers and industry groups, working on various committees and writing papers for numerous industry publications. Over his career, he has published many articles in magazines, technical journals and publications and more recently in 2007 he proudly served as Technical Director for the Electroless Nickel Conference '07.

Brad joins Coventya, Inc., at their technology center in Cleveland, Ohio.

Test Your Plating I.Q. #442

By Dr. James H. Lindsay

Regulation Protocols

What do the following acronyms mean and what do they concern?

1. REACH
2. RoHS
3. WEEE
4. GHS
5. ELV
6. WHEEE (Extra credit)

Answers on page 46.

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U.S. EPA, *Granular Activated Carbon Absorption & Regeneration*, U.S. EPA No. 832-F-00-017, U.S. EPA, Washington, D.C. 2000; http://www.epa.gov/owmitnet/mtb/carbon_absorption.pdf

Water Environment Federation, *Design of Municipal Wastewater Treatment Plants*, MOP 8, 4th Ed., Water Environment Federation, Alexandria, VA, 1998.

Calgon Carbon Corp., P.O. Box 7171, Pittsburgh, PA 15230-0717.

C-H. Huang, "Effective Removal of Organics from Nickel Wastewater by Modified Carbon Adsorption," *Plating & Surface Finishing*, **79** (4), 50 (1992).