What to Do with Toxic, Contaminated Cellulose-based Adsorbents

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This editorial considers the end fates of toxic materials, such as heavy metals, dyes, and synthetic organic compounds, which can be recovered from polluted water by using bio-based adsorbents. The point of the editorial is that insufficient research attention has been paid to the final fate of such contaminants. By contrast, much is known regarding factors affecting the adsorption capacities and rates of adsorption onto cellulose-based materials. Highly contaminated solutions are produced during the regeneration of biosorbent materials. Eutectic freeze crystallization potentially could be used to isolate relative pure compounds of heavy metals from such solutions. Alternatively, biochar can be prepared from cellulosic material in such a way as to achieve strong attachment to certain pollutants. Such biochar, after its use as an adsorbent, could be placed in the ground, where it can be expected to remain stable as sequestered carbon. A high ion exchange capacity of such biochar has potential to reduce the rates of leaching, which could otherwise lead to contamination of groundwater near to landfill sites. As shown by these examples, some promising answers to the final fate of contaminants may conform to a "circular economy" model, whereas other promising answers may conform to a "cradle-to-grave" viewpoint.

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Biosorption of Pollutants – An Incomplete Answer

Cellulose-derived adsorbent materials are often proposed as a promising option to remove pollutants from contaminated water. Although there are countless published articles documenting the success of such adsorption strategies (see Hubbe *et al.* 2011, 2012, 2013, 2014), the ultimate fate of the contaminants is seldom addressed in the published articles. Some authors document the regeneration of biomass-based adsorbent materials, for instance by exposing them to a salty brine or low pH water, *etc.*, thus causing the pollutant, *e.g.* a heavy metal ion or a dye, to be released. However, such procedures merely place the pollutant back into an aqueous solution, leaving the ultimate fate of the pollutant still unresolved.

It is proposed here that more research attention needs to be paid to identifying and perfecting promising strategies related to the final fate of such pollutants as heavy metals, synthetic dyes, and toxic organic compounds. Such work can be expected to face great challenges. In typical cases, the contaminated cellulose-based adsorbent will contain too much water to be suitable for landfilling, which in any case would involve concerns about leaching of the contaminants into groundwater. Many districts have prohibitions against the use of incineration as a means of dealing with strongly metal-contaminated materials (Linak and Wendt 1993).

Used Biosorbents Loaded with Organic Contaminants

In the case of organic contaminants, one of the key routes to consider is biological degradation. This can involve such options as composting, or even conventional secondary wastewater treatment with the use of aeration and activated sludge. Another option, though conflicting with a point made in the previous paragraph, may be incineration. To deal with hard-to-degrade organic compounds such as lignin decomposition products and other phenols, advanced oxidation strategies such as ozone, Fenton oxidation, or TiO_2-catalyzed UV irradiation, can be carried out as pretreatments before biodegradation steps (Hubbe *et al.* 2016).

High-temperature pressurized treatment, *i.e.* hydrothermal treatment, can be another way to break down organic chemicals and render the mixture for suitable for biodegradation as a means to decrease the biological oxygen demand (BOD) and toxicity of the treated water. Hydrothermal processing, because it does not require a phase change of the water present in a contaminated material, represents a relatively low-energy way to break down recalcitrant organic compounds. By the use of pressurized conditions, boiling is suppressed, while at the same time the temperature becomes high enough so that the molecules frequently reach various transition states related to their potential decomposition into benign and more readily biodegradable forms (Kruse *et al.* 2013). The treated mixture then can be used to generate and collect a higher amount of methane, which has value as a fuel, in a subsequent anaerobic digestion step (Pages-Diaz *et al.* 2020).

Used Biosorbents Loaded with Heavy Metals

When metals are the main contaminant in cellulose-based adsorbents, after their use, research is needed to find the most promising way to convert various brine concentrates, often obtained in the course of regeneration of the adsorbent materials, back to isolated compounds, which might have potential value. In principle, this can be accomplished by a process called eutectic freeze crystallization (EFC) (Randall *et al.* 2011; Hubbe *et al.* 2018). Though EFC has been demonstrated as an effective and energy-efficient method, the amount of published work is relatively little. It is known, for instance, that certain inorganic compounds can be separated from each other, as solid materials, by careful application of ERC in stages and different temperatures. The purity can be increased by adding seed crystals (Aspeling *et al.* 2020). However, it has not been shown yet that EFC can be applied to complex mixtures that contain multiple dissolved metal species as well as other contaminants.

A Stretch Goal to Recover Each Contaminant in Pure Form

Visionaries have proposed usage or the term "circular economy" to describe a world in which humans can thrive for many years without damaging the biosphere or depleting the resources. Part of such a system would require ways to re-use even the most dilute and toxic components of the byproducts and wastes of the many unit processes that together make up the technology that supports us in our daily lives. Much attention has been paid to some steps that are needed in creating a circular economy, such as adsorbing contaminants from water, by the use of cellulose-derived adsorbent materials. However, the work cannot be regarded as being complete. Difficult steps remain to be resolved regarding the final fate of toxic substances such as heavy metals, dyes, and other recalcitrant compounds that become collected onto such adsorbents as biomass, biochar, and lignocellulose-derived activated carbon.

A Fallback Goal to Hold Contaminants So That They Do No Harm

When practitioners of Life Cycle Assessment set out to do a comprehensive analysis, the term “cradle-to-grave” is often employed. In order for that term to be valid, the end state must indeed represent a stable condition, without significant further harm to the environment continuing. For instance, two kinds of harm can be expected if a contaminated biomass-based adsorbent is merely buried in the ground. On the one hand, most plant-based materials are likely to decay anaerobically in the buried environment, which may be moist and airless. Such decay will likely result in evolution of methane gas, thereby contributing to global warming if it is not completely collected (Bolan *et al.* 2013). Meanwhile, leaching may lead to contamination of groundwater with heavy metal ions or with toxic organic compounds. It turns out that both of these problems can be addressed. By pyrolysis of biomass at temperatures in the range from about 500 to 800 °C, for optimized times, the material can be converted to biochar. Such conversion tends to increase the hydrophobic character of the material, which can lead to stronger association with some organic contaminants of concern, such as phenols (Oh and Seo 2016; Komnitsas and Zaharaki 2016). By adjusting the conditions of pyrolysis, it is also possible to increase the ion exchange capacity, so that the resulting biochar holds more tightly onto the metal ions (Ahmad *et al.* 2014). Biochar has the further advantage of being quite stable to further biodegradation, so that it generally is not associated with methane generation, and it sequesters carbon (Mukherjee and Lal 2013). So in cases where procedures associated with a true circular economy have not yet been demonstrated, an optimized cradle-to-grave” strategy may be regarded as the next best thing.

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