New Horizons for Use of Cellulose-Based Materials to Adsorb Pollutants from Aqueous Solutions

Martin A. Hubbe

This article reviews recent research related to biosorption – the use of plant-derived materials to remove various pollutants from aqueous systems. Emphasis is placed on biosorption studies dealing with the removal of heavy metal ions, dyes, and spilled oil from water. Much progress already had been achieve in understanding the factors that affect adsorption capacities, rates of uptake, and possible release back into the water. It has been shown that the performance of cellulose-based sorbent materials often can be improved by physical of chemical modification of the sorbent. There is a critical need for research related to strategies for dealing with the adsorbent materials after their use. In addition to regeneration and re-use of sorbent materials, attention also needs to be paid to the incineration of contaminated sorbents, as well as the biodegradation of sorbent material after uptake of various pollutants.

Contact information: Department of Forest Biomaterials, North Carolina State University, Campus Box 8005, Raleigh, NC, USA 27695-8005; hubbe@ncsu.edu
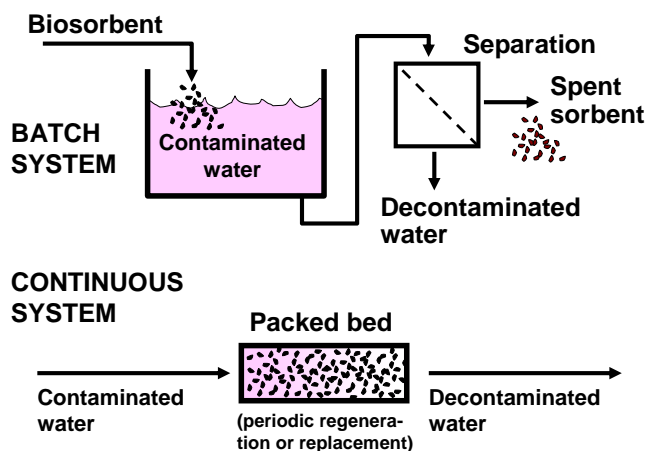
INTRODUCTION

The term "biosorption" has been widely used to describe systems in which plant-derived materials are used to remove various pollutants from aqueous systems. This article reviews research related to the adsorption of three important categories of pollutant: heavy metals, dyes, and spilled oil. In each case there has been an acceleration of interest within the scientific community, resulting in numerous publications. Also, in each case there is evidence that the effectiveness of water cleanup can be enhanced by physical or chemical modifications of the cellulosic material in many cases.

This article will make frequent references to a series of more narrowly focused review articles dealing with biosorption of heavy metals, dyes, and oils, respectively (Hubbe *et al.* 2011, 2012, 2013). Each of the cited articles includes extensive tabulation of the main findings presented in published articles up to that point in time. In addition, other recently published primary literature will be cited, showing advances in the state of knowledge concerning biosorption of metals, dyes, and spilled oils.

Two main approaches used in biosorption for the removal of contaminants from water are illustrated in Fig. 1. In batch operations it is usual for the sorbent material to be added to an agitated volume of the solution to be treated. In a subsequent operation the mixture is filtered to remove the sorbent, with the goal of producing decontaminated water. In flow-through or "packed bed" systems the sorbent material is held in place, while the water to be decontaminated is passed through it. The process is continued until

the concentration of contaminant in the emerging stream begins to rise. At that point the sorbent material is either replaced or regenerated.

Fig. 1. Schematic representations of two main schemes used for biosorption of pollutants from contaminated waters

To a large degree, the step of getting the target pollutants to adsorb onto the surfaces of cellulosic materials – and thus get them to be removed from the water – has already been solved through use of a wide range of plant-derived byproducts, either as-received or in chemically modified form. Modification strategies, including not only chemical modification but also mechanical treatments, torrefaction, pyrolysis, and activation of carbonaceous byproducts from cellulosic materials have been shown to increase the sorption efficiencies in numerous cases (Babel and Kumiawan 2003; Dias *et al.* 2007; O'Connell *et al.* 2008; Hubbe *et al.* 2012). However, the fact remains that biosorption technology is still very far from being fully implemented at an industrial or municipal level. Clearly there are some practical as well as theoretical barriers that are inhibiting the deployment of systems that have appeared highly promising according to the results of many academic studies.

KEY CHALLENGES FACING BIOSORPTION TECHNOLOGIES

The toxic nature of various water-soluble metal species, various dyes, and various spilled oils have been shown in past work (Aguilera *et al.* 2010; DeLaune and Wright 2011). Despite efforts to minimize such releases, the accelerating development of modern technology has tended to increase the amounts of such toxins in the worlds waterways and supplies of fresh water intended for various applications.

When academic scientists are looking for suitable topics by means of which to train the next generation of researchers, biosorption studies can appear to offer many attractive features. In the first place, idealistic students appreciate the opportunity to devote their efforts to the resolution of important environmental problems. Secondly, such efforts can be focused on whatever types of industrial pollutants that happen to be

prevalent in a given region. Likewise, the work can be presented as a way to make advantageous use of selected regionally available cellulosic byproducts that somebody has regarded as "waste". In the course of modifying the cellulosic substrate, students can learn some advanced chemical strategies, various statistical analysis methods, the use of rate expressions, and concepts related to adsorption isotherms. As a result of this combination of favorable circumstances, there has been an outpouring of individual studies of biosorption, and there has been a seemingly almost random pairing between the target pollutants and the nature of the biosorbent materials considered in different studies. In view of the great amount of work already done, this appears to be a good time to address some critical challenges that may be slowing down the pace and effectiveness of implementation of bioremediation technologies at a commercial level.

The Diverse Nature of Natural Cellulosic Materials

A key challenge, which appears often to have been overlooked in the course of studies of biosorption of pollutants, involves the huge diversity of naturally available cellulosic materials, as well as their underutilized byproducts. Even before any steps have been taken to modify the absorbent material, past studies have shown differences as large as a factor of 1000 in the adsorption capacities for selected metals or dyes (Hubbe *et al.* 2011, 2012). Given the existence of such huge ranges, one needs to be skeptical that a given chemical or physical processing step can be justified in a given case. To give an example, untreated kapok has been found to be a superb sorbent for spilled oils (Choi and Cloud 1992; Lim and Huang 2007); in fact the performance of unmodified kapok for oil sorption is already in a similar range to that of polypropylene fibers, which are the most widely considered sorbent for such applications (Hubbe *et al.* 2013). Similarly, when collecting cationic dyestuffs from water, various unmodified cellulosic materials meet or exceed the performance of specialized sorbents, such as activated carbon products (Aksu *et al.* 2010). Again there is a difference by a factor of about 1000 in adsorption capacity between the most and least effective unmodified cellulosic material used from removal of cationic dyes from water (Hubbe *et al.* 2012).

Various factors are likely to account for some of the great differences in adsorption capacity obtained by different researchers carrying out nominally similar studies. The accessible surface areas, per unit mass, might differ by large amounts, depending on the conditions or preparation. The chemical nature of the surfaces may differ substantially as well. In principle only a monolayer of material on a surface can profoundly change its affinity for different kinds of sorbate molecules. For instance, the presence of carboxylate species at the fiber surface is sometimes well correlated to the uptake of cationic metal species from solution (Xei *et al.* 1996; Foglarova *et al.* 2009; Klasson *et al.* 2009; Hubbe *et al.* 2011), and such a relationship can provide evidence of an ion exchange mechanism (Gadd 2009). Such carboxylate groups might be present on minor components such as certain hemicellulose species, or certain extractable fatty acids, *etc.* Likewise, the lignin component of the substrate, to the extent that it is exposed at the surface, might be important for sorption of sparingly soluble substances such as dyes and oils (Lebek and Wardas 1996; da Silva *et al.* 2011; Kriaa *et al.* 2011).

Cellulosic material can be modified in many ways to improve its performance in various applications. Some modifications that are most widely reported for increasing

the performance of biosorbents are aimed at increasing the amount of surface area that is accessible by the target pollutant. One of the great challenges facing technologist involves the large amounts of energy that often are required to open up cellulosic materials and to make their interior surfaces more accessible. Take, for example, the conversion of wood to chips. The amount of energy to achieve such a conversion is of the order of 2 to 4.5 kJ/m^3 (Lusth *et al.* 2013). If one takes the wood density to be approximately 0.5 metric tons per m^3, these values correspond to 1.3 to 2.5 X 10^{-3} kWh/t. Further reduction of biomass to powder form was estimated to require 47 to 91 kWh/t (Sun *et al.* 2011), which is a huge amount of energy. Fortunately, a prudent technologist or entrepreneur has the option of collecting sawdust as an underutilized byproduct from a sawmill. Another approach is to use cellulosic materials that are inherently porous or finely divided, *e.g.* the spent material from fermentation processes (Svecova *et al.* 2006; Park *et al.* 2008a; Vijayaraghavan *et al.* 2008) or other microbial material (Ahluwalia and Goyal 2005; Bishnoi and Garima 2005).

One of the simplest ways to change the surface nature of cellulosic materials is to heat it up. Moderate heating (say up to 210 $^{\circ}$C) can promote migration of low-surface-energy material such as waxes to the accessible surfaces (Dundar *et al.* 2012; Kutnar *et al.* 2013). Stronger heating in the absence of oxygen leads to torrefied products, for which surface properties have been studied (Stelte *et al.* 2012). Finally, heating in the range of 500 to 900 $^{\circ}$C for controlled time periods in the absence of oxygen can convert the material essentially to carbon. Post-treatment of the carbonized biomass, using KOH, phosphoric acid, or steam, among other options, can greatly increase the internal porosity; products made in this way are called "activated carbons" (Chowdhury *et al.* 2013). All of these heat-processed materials, if carefully optimized, can greatly increase the uptake of various pollutants.

To complete the story, modifications involving chemical agents can change the surface chemistry of sorbents in highly controllable ways. For example, reactions with various anhydrides provide a convenient way of grafting various functional groups onto the hydroxyl groups of cellulosic materials (Chandlia *et al.* 2009; Karnitz *et al.* 2010). Also, cellulose-based surfaces can be carboxymethylated (Xie *et al.* 1996). By judicious selection of the non-reactive end of the agent used for derivatization, it is possible to achieve a wide range of charged character (including positive or negative charge) as well as degree of hydrophobic or hydrophilic character.

Modeling and Quantification of Pollutant Uptake

Increasing levels of sophistication have been reached by researchers in their use of theoretical models to interpret the kinetic and equilibrium aspects of their biosorption studies (Hubbe *et al.* 2011, 2012). The majority of the data sets considered in the cited articles have been found to fit adequately to a Langmuir adsorption isotherm (Langmuir 1918), which assumes a fixed number of equivalent adsorption sites. Many authors have explored alternatively models. The fact that certain data sets have been better fitted to the Freundlich equation (Freundlich 1907) can be taken as evidence of heterogeneity of adsorption sites, at least in those cases. Some authors have drawn mechanistic inferences based on fits of adsorption isotherms using models such as the Redlich-Peterson Isotherm (Padmesha *et al.* 2006), or multiple-species versions of the Freundlich or Langmuir

models (Fritz and Schlünder 1974; Aksu *et al.* 1997). Such attempts need to be viewed with caution. In many such studies the data were found to simultaneously achieve good fits ($R^2 \gg 0.9$) to more than one theoretical model (Hubbe *et al.* 2011), and the default interpretations from the different models can be quite different from each other. This type of problem in interpretation deserves careful study, possibly using new experimental approaches to shed fresh light on the underlying mechanisms.

Similar challenges, involving competing possible interpretations, face those investigators working to better understand the rates of uptake of pollutants onto cellulose-based sorbents. The most widely used models for fitting kinetic data from such experiments are a first-order diffusion model (Lagergren 1898), a pseudo-second-order model (McKay and Ho 1999; Ho *et al.* 2000), and an inter-particle diffusion model (Weber and Morris 1963). Of these three, a surprisingly large proportion of data sets appear to be best described by the pseudo-second-order model. There seems to be no consensus among researchers regarding what the good fits of data to the pseudo-second-order model imply about the underlying mechanism. The form of the equation would seem to imply that pairs of groups bound to the substrate need to simultaneously and independently diffuse and collide with the adsorbate species in the rate-controlling step (Hubbe *et al.* 2012). The literature appears to be silent regarding how such a mechanism could possibly be to a valid description of what happens at fixed sites on a solid substrate. Fortunately, there is a quite different way to explain why a pseudo-second order model should be so successful in modeling the sorption isotherms of various heavy metals and dyes. The form of the equation is consistent with a sharply decreasing opportunity for the last available adsorption sites to be filled as the sorbent reaches saturation. Thus, the model is a good one for cases in which the last-to-be filled sites are increasingly less well suited for the adsorbate, either due to spatial constraints or due to an accumulation of excess electrostatic charge due to adsorption of other ionic adsorbate molecules.

Another issue that seems to have received insufficient attention is the effectiveness of different sorbents to reduce levels of water-borne pollutants to extremely low levels. Ideally one would prefer sorbents having a favorable combination of high sorption capacity and high affinity, allowing the residual concentration in the solution to be kept at a very low level even after quite a high amount of the pollutant has been adsorbed. One of the key concerns, in this regard, is that typical adsorbents are likely to have a wide variety of surface sites – some offering high affinity for the pollutant, and some offering lower affinity. The higher-affinity sites would be the most likely to become filled relatively early in the process of biosorption. Because the remaining sites would be lower in affinity, one would expect there to be a higher bulk concentration of pollutant once the system reaches equilibrium. Though certain researchers have attempted to model such situations, for instance by use of a multiple Langmuir model with several classes of sites (Sheng *et al.* 2007; Hubbe *et al.* 2011), there is clearly a lot more to be done from a practical perspective.

Certain potentially favorable strategies for water treatment deserve to be evaluated at the lab scale. For instance, one can envision a system in which two packed beds of adsorbent material are used in series. Presumably the first bed would be selected having a high capacity for adsorption. The second one would be selected based on having a very high affinity for the pollutant and an ability to decrease the bulk

concentration almost to zero. Such systems could be compared in the lab to either type of bed by itself or to mixed beds in which the two sorbent materials are used together. Some of the equations that would be needed to interpret results of such work already have been demonstrated (Malkoc *et al.* 2006; Xiu and Li 2000).

Though quite many researchers have studied competitive adsorption among two or more dissolved species, most such work has involved competition between pollutants quite similar to each other. For instance, the following cited studies evaluated the adsorption of mixtures of different cationic metal ions onto cellulose-based sorbents (Ho and McKay 1999; Leyva-Ramos *et al* 2001; Aksu and Donmez 2006; Srivastava *et al.* 2006). Likewise, the following studies evaluated simultaneous removal of pairs of relatively similar dyestuffs from a mixed solution (Porter 1993; Al-Degs *et al.* 2007). An inherently more challenging situation is when contaminated water contains, say, a cationic metal species (*e.g.* Pb(II) or Ni(II)) and an anionic species, such as the chromate ion (Aksu *et al.* 2002). The cationic species are often removed most effectively at a near-neutral pH, whereas pH values of 1 to 3 are often required in order to achieve effective adsorption of the anionic chromate (Hubbe *et al.* 2011). Further studies need to address practical concerns for the simultaneous or sequential removal of multiple species, as would be expected in the outfalls of many industrial processes.
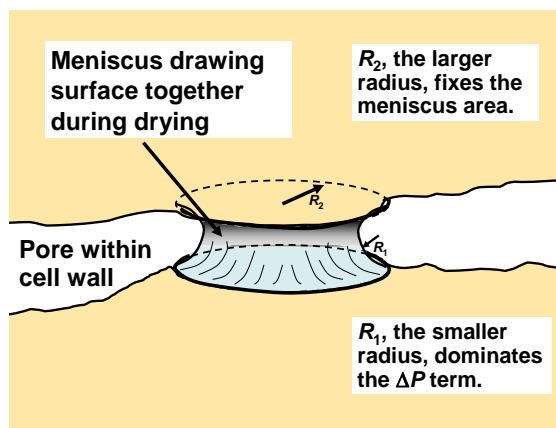
Environmental Costs of Cellulose Modifications

Each time that a natural material needs to be modified, in preparation for a specified use, one can expect there to be an increase in the overall cost. Also, the amount of energy expended and other adverse environmental consequences will tend to increase. For these reasons, one of the major challenges that faces both researchers and policy-makers involves how to quantify and minimize net environmental impacts. Some notable recent progress can be cited (de Hoces *et al.* 2011). Some of the main strategies that can be used to minimize greenhouse gas emissions and other adverse environmental impacts related to bioremediation include the following:

- Local sourcing of materials, thus minimizing the costs and energy requirements associated with transporting the sorbent
- Bypassing or minimization of non-essential processing steps that use non-renewable energy
- Avoidance of procedures that require use of solvents, especially if the solvents are not efficiently recycled or transformed into energy during the process
- Avoidance of such landfilling practices that are likely to result in generation of methane due to the anaerobic decomposition of spent absorbent material

Avoidance of unnecessary drying steps may be considered to be one of the most important challenges that will required research attention in the coming years. Tabulation of experimental conditions used in studies involving the biosorption of metals and dyes (Hubbe *et al.* 2011, 2012) has revealed surprisingly strong preferences among researchers to thoroughly dry their sorbent material before its use. Such a preference is probably motivated by concerns about the storage stability of wet or damp cellulosic material. Also, a researcher would want to standardize the starting material in some way. But drying requires a high energy input.   It also entails risk of closing up pores within

the material, thus reducing the accessible surface area that is available for adsorption of the pollutants (Stone and Scallan 1966).

The way that pore closure comes about during a typical drying process is illustrated in Fig. 2. The figure envisions a slit-like pore within the material before drying. As shown, during the evaporation of water from cellulosic material one can expect there to be a meniscus formed between adjacent cellulosic surfaces.

Fig. 2. Schematic representation of a meniscus of water tending to draw surfaces together within a slit-like pore of the cellulosic material during drying

Because of the surface tension at the air-water interface, and due to the curvatures of the liquid surfaces, the pressure inside of the film of water can be much lower than the ambient pressure. In other words, a tension or "vacuum effect" exists within the liquid, drawing the two surfaces together. The maximum pressure difference can be estimated from the Young-LaPlace equation (Page 1993; Chen *et al.* 2006),

$$\Delta P = 4 \gamma \cos\theta \ (1/R_1 + 1/R_2) \tag{1}$$

where γ is the air-water interfacial tension, θ is the contact angle as measured through the liquid phase, R_1 is the smaller radius of the meniscus, and R_2 is the larger radius. After making some simplifying assumptions, such as setting the contact angle to zero (to represent the case of perfect wetting), Eq. 1 can be approximated as,

$$\Delta P \approx 2 \gamma / x \tag{2}$$

where x is the thickness of the film of water. Since x is in the denominator of Eq. 2, the predicted pressure difference tends toward infinity as x tends toward zero. Though the assumptions underlying the use of Eq. 2 are sure to break down long before an infinite force is reached, the existence of extremely strong forces has been shown by structural damage to surfaces that have been dried in contact (Stratton and Colson 1993).

Another practice that needs to be re-examined is the grinding of cellulose-based material before its use as a sorbent. Grinding requires energy. In addition, grinding converts the material into fine particle that may slow down the flow through a packed bed

that is being used to remove pollutants from water. Alternatively, if the absorbent is mixed into the polluted water as a suspension, then the finely suspended particles may be more difficult to remove from the liquid by settling or filtration. The reason why researchers have preferred the use of ground materials may be due to concerns about the uniformity of samples, especially when the scale of laboratory experimentation may be small. Also, it is logical for a researcher to expect that grinding would increase the external surface area, thus increasing the sites available for adsorption. The problem with using such logic is that the most effective sorbent materials tend to be porous, and adsorption may take place mainly on internal surfaces – not just on the outside. There is an urgent need for research dealing with the practical optimization of particle size with respect to flow rates, separation steps, and also with the final processing of biosorbents after they have been used.

What to Do with Used, Contaminated Sorbent Material

One of the least-resolved aspects of biosorption involves the question of what to do with the cellulose-based sorbent material after it has been used. An effort was made to discover any articles dealing with this issue during preparation of recent review articles (Hubbe *et al.* 2011, 2012, 2013). Only about 20% of the reviewed articles, dealing with the topic of bioremediation, paid any attention at all to the subsequent fate or handling of the sorbent material after its use. Of that 20%, most merely reported on the reversibility of sorption when changing the pH conditions or some other treatment to reduce the affinity of the substrate for the adsorbate.

Landfilling, *i.e.* the placement of waste materials in the ground, has been regarded as the most likely destination of various contaminated materials (Carro *et al.* 2008). Motivations for landfilling of spent sorbent materials could include relatively low cost and expediency. Unfortunately, landfilling happens to be poorly suited to the disposal of cellulose-based materials, which can be subject either to anaerobic decomposition or leaching. The generation of greenhouse gases such as methane can be expected when cellulose and related materials are kept in a moist, non-aerated environment (Padgett 2009). In terms of global warming, methane gas is about 21 times as harmful as carbon dioxide (EPA 2013), though the predicted effects have been disputed due to differences in the persistence of different gases in the atmosphere (Shoemaker and Schrag 2013). While state-of-the-art landfill facilities attempt to collect such gases (Kumar *et al.* 2011), there is a wide range in practices and equipment by which such systems are implemented.

Reversibility of sorption – for what purpose?

In principle, the "regeneration" of a material, allowing it to be used multiple times for the same purpose, would tend to be considered as a positive attribute of the process as a whole. However, each such application needs to be considered from a viewpoint of minimizing the net adverse environmental impact. Suppose, for instance, that a cellulose-based substrate is immersed in a strongly acidic solution to bring about the release of heavy metal ions such as Pb(II) (see for instance Martínez *et al.* 2006). Under such conditions, all of the carboxylic groups on the substrate become protonated, causing cationic adsorbates such as Pb(II) become displaced back into the solution. In favorable

cases the sorbate can be restored nearly to its uncontaminated state, and its sorption capacity can be almost completely restored as well.

Not a single author, out of all of the hundreds of articles considered in the series of three review articles (Hubbe 2011, 2012, 2013) attempted to explain and justify the logic of why it could make sense to collect metals, dyes, or oil from water and then to turn around and change the conditions to put those same materials back into water again. Presumably, by optimization of procedures, it may be possible to achieve a much higher concentration of metals or dyes, *etc.*, compared to the original effluent to which the sorbent was applied. And maybe, despite a lack of supporting documentation in the published literature, there are ways to extract value from such relatively more concentrated solutions of metals, dyes, or oils. Readers who have an appetite for working with toxic mixtures, especially if they can find ways to extract valuable components from such mixtures, are likely to find relatively little competition from other researchers. The challenge that one is likely to face, in addition to such factors as toxicity, extremes of pH, and still rather dilute solutions, is that one can ordinarily expect to be dealing with variable mixtures. In the case of mixtures of dyes, it may be difficult indeed to propose any practical usage of the recovered material.

Since the adsorption step is key to the process as a whole, the following three sections will deal with adsorption of metal ions, dyes, and oils, respectively. Each of these sections will focus on how various modifications of cellulose-based sorbents have been found to affect uptake of pollutants in each of the three cases. Subsequent sections will deal with incorporation of biosorption into a practical cradle-to-grave scenario in which the fate and processing of each component needs to be considered.

BIOSORPTION OF METALS, DYES, AND SPILL OIL

Metals Uptake and Effects of Cellulose Modifications

As discussed at greater length elsewhere, one of the most promising situations for use of cellulose-based sorbents can involve a polishing treatment to remove heavy metal ions from dilute aqueous solutions (Hubbe *et al.* 2011). Other strategies, such as chemical precipitation, distillation, and reverse osmosis (Fu and Wang 2011; Li *et al.* 2012; Plappally and Lienhard 2012), can make sense when dealing with relatively concentrated solutions of metals, either to minimize the volume of waste material or to convert it to a solid, more easily storable form. Relative to the other approaches listed, biosorption appears to be well suited to working with highly dilute solutions. Two situations likely to be especially promising for potential applications are (a) the final treatment of wastewater before its release (after primary clarification to removal solids and activated sludge treatment to remove biological materials), and (b) treatment of fresh water to remove traces of toxic metals. Regulations and health concerns can influence the levels of metals deemed acceptable in each of these two cases.

Most systems involving biosorption of metal ions can be understood in terms of the principles of ion exchange (Gadd 2009). In other words, one envisions each adsorbing metal ion as displacing a number of other ions, such as sodium or hydrogen, corresponding to the valence of the metal species. Ion exchange mechanisms are thus

able to explain such things as the tendency of adsorbed amounts to be constrained by a saturation level. Also, an ion exchange mechanism is consistent with an ability to reverse the process, thus regenerating the adsorption ability of the substrate, by addition of a high concentration of the initially present ions, *e.g.* immersion in a salt brine. In the case of positively charged metal ions, ion exchange can be used to explain why a reduction in pH tends to displace such ions from the substrate. What happens is that the metal ions' ability to adsorb becomes overwhelmed by the much higher concentration of competing monovalent H_3O^+ ions.

A complication arises when considering metal ionic species having negative charge. The most widely studied and important example is the chromate ion, CrO_4^{2-} (Agrawal *et al.* 2006; Mohan and Pittman 2006). If one assumes that the chromate ion remains in its anionic form throughout an adsorption process, it is then difficult to understand why it would tend to adsorb onto cellulosic substrates, which generally have net negative surface charge at pH values greater than about 2.5. In fact, the highest efficiencies of adsorption of the chromate ion generally are observed at pH values in the range of about 1 to 3 (Gupta *et al.* 1999; Malkoc and Nuhoglu 2007; Hubbe *et al.* 2011). At such low pH values the carboxyl groups at a cellulosic surface are essentially all protonated, and protonation of some hydroxyl groups at extremely low pH appears to be part of the mechanism.

A further complication arises due to the fact that the chromate ion is a strong oxidizing agent, and cellulosic surfaces are susceptible to oxidation. Studies have shown convincingly that adsorption of the chromate ion often entails simultaneous oxidation of such surface groups, leading to the formation and adsorption of the trivalent Cr^{+3} species, for which the maximum adsorption capacity is at a higher pH (Park *et al.* 2008a).

Because various carboxyl groups at cellulosic surfaces have pKa values in the range of about 3.5 to 6, it makes sense to expect that the adsorption of cationic metal ions ought to increase steadily with increasing pH. Many studies have shown such behavior within acidic pH ranges (Hubbe *et al.* 2011a). However, a maximum uptake is often observed somewhere within the pH range of 5 to 8, and beyond that maximum the uptake falls steeply. The usual explanation is that multivalent metal cations can form neutral hydroxide species at those higher pH values (Demirbas 2008). Despite the ubiquitous nature of this phenomenon, there appears to have been very little research attention devoted to isolation of such hydroxylated neutral metal species, possibly as a mechanism for their removal from solution.

Many studies have explored effects of temperature on adsorption of metal ions onto cellulose-based substrates. In cases where the adsorption decreases with increasing temperature, such findings have been used as evidence for an exothermic nature of the adsorption. In other words, heat is given off as the metal ions become adsorbed. But in a great many cases, the situation has been found to be the reverse, with increasing adsorption capacities in response to increasing temperature of equilibration. The latter systems can be described as endothermic. In such cases the process still can occur spontaneously due to the increasing freedom of motion experienced by the monovalent ions released from the surface in the course of adsorption, *i.e.* due to increased entropy (Rao *et al.* 2012).

Because negatively charged surface groups at adsorbent surfaces clearly help in the adsorption of cationic metal ions from aqueous solution, investigators have explored many means of increasing the population of such groups (Hubbe *et al.* 2011). For example, the amount of carboxylate groups at a cellulose-based surface often can be increased by oxidation (Klasson *et al.* 2009), carboxymethylation (Xie *et al.* 1996), or succinylation (Chandlia *et al.* 2009) reactions, among others. In such cases, large increases in metal uptake have been documented (Hubbe *et al.* 2011). Even greater effects have been achieved by grafting cellulosic surfaces with highly carboxylated polymer chains (O'Connell *et al.* 2008). The cited results are consistent with the ion exchange mechanism described earlier. In addition, the presence of multiple carboxylic groups in close proximity to each other make it important to consider the involvement of chemical complexation as an important contributing mechanism. In such cases, each metal ion may be associated with more than one carboxylate group as a ligand. By analogy to efficient chelating agents such as ethylenediaminetetraacetic acid (EDTA), one can expect to achieve a very high affinity of cationic metal ions to such surfaces (Gyurcsik and Nagy 2000). It follows that the use of highly carboxylated surfaces is a useful strategy when the goal is to reduce the solution concentrations of metal ions to very low levels.

Another important way to modify cellulosic materials in an attempt to improve their ability to adsorb various pollutants is by heating them strongly. The results of such treatment fall within a wide range depending on the intensity of the conditions used. Relatively mild conditions of treatment, with temperatures up to 150 $^{\circ}$C, are classified as "drying". The term "torrefaction" is used in an intermediate range of temperature, usually with the exclusion of oxygen to avoid combustion (Chew and Doshi 2011). When cellulosic materials are exposed to high temperatures, *e.g.* 400 $^{\circ}$C to about 900 $^{\circ}$C, the process is called "pyrolysis" or "carbonation" (Chowdhury *et al.* 2013). As implied by the latter term, the composition of the material becomes enriched in carbon, whereas the amounts of hydrogen, oxygen, and traces of other elements tend to be reduced in the carbonized material. To further enhance the ability of carbonized matter to adsorb pollutants, the material is activated, a process in which the nanoscale porosity is developed and optimized (Chowdhury *et al.* 2013). Activation involves strong heating in the presence of such substances as phosphoric acid or KOH. Steam, carbon dioxide, and various other treatments also can be incorporated into activation processes.

Although it can be said that high surface area tends to maximize adsorption capacity for various pollutants, it can be equally important to speed up the rate with which pollutant molecules can gain access to sites within an activated carbon material. Thus, conditions of preparation (temperatures, times, concentrations of activating species, *etc.*) are optimized to yield a favorable mixture of micropores (< 2 nm), mesopores (2 to 50 nm), and larger pores (> 50 nm) to facilitate relatively rapid diffusion of species into the porous structure, while still providing the huge specific surface areas (*e.g.* as high as about 1000 m^2/g) associated with material incorporating the smallest micropores. Though activated carbon species have been found to be highly effective for adsorption of metal ions, it is important to bear in mind that similar levels of metal uptake have also been achieved by use of other kinds of cellulose-based sorbent materials (Baillet *et al.* 1998; Loukidou *et al.* 2004; Hubbe *et al.* 2011).

There has been a moderate level of research aimed at adjusting the surface chemistry of cellulose-derived carbonaceous material for purposes of increasing the adsorption of certain metal species (Lyubchik *et al.* 2004; Chowdhury *et al.* 2013). This type of research is challenging due to the fact that any chemical change is likely to also affect the distribution of pore sizes, surface areas, and other features of the material. Also, attempts to introduce acidic groups onto the surface of activated carbon can be expected to lead to oxidation of the material in general, even causing its combustion if the conditions are pushed too far. While various results have been promising for enhancing metal adsorption performance, this is an attractive area for future research.

Torrefaction deserves greater attention in future studies. The yield of torrefied material from a given amount of biomass is much higher than the yield of activated carbon. Though torrefied wood cannot be expected to allow development of nearly as high specific surface areas as activated carbon products, the torrefied samples can be expected to have a great diversity among their surface chemical sites. Torrefied products also are more likely to retain pore structures associated with their origin as cellulosic materials, and this may be potentially advantageous; however very little work of this type has been reported.

Dye Uptake and Effects of Cellulose Modifications

Water-soluble dyestuffs present in industrial streams and waterways are of concern not only because of possible toxicity, but they are highly colored, difficult to remove by conventional wastewater treatment, and often quite resistant to biodegradation (Rai *et al.* 2005). Common dyestuffs tend to be somewhat hydrophobic, which can be a great advantage when one wants to collect them onto a suitable absorbent from aqueous solution. The aromatic groups and conjugated double bonded structures within industrial dyes do not have a natural affinity for water, except that many dyes have been synthesized with enough hydrophilic groups to permit their effective distribution onto the material to be dyed. Another characteristic of the most common dyestuffs is that they are predominantly organic materials, with only a small proportion of metal, if at all.

As in the case of adsorption of heavy metal ions, studies of dye uptake have shown huge variations – even when the nominal conditions may be very similar (Hubbe *et al.* 2012). It follows that there must be subtle differences in the way the experiments were conducted. In particular, the cellulose-based substrates appear to have been handled differently, perhaps even before their acquisition by the researchers. So, one challenge for enterprising researchers in the future will be to gather fresh, never-dried materials from the selected field, woods, or waste stream and to closely control each step during storage, optional drying, and other processing steps.

One of the next challenges to consider, relative to biosorption, entails the diverse nature of dyestuffs and the fact that an effluent stream may contain a mixture of them. The most widely used dyes used in textile manufacture can be classed as reactive, direct, acid, basic, or sulfur dyes, among others (Hunger 2003; Hubbe *et al.* 2012). Of these, only the basic dyes have a positive charge, which provides a natural electrostatic attraction onto the typically negatively charged surfaces of cellulose-based materials. Many studies have addressed the relative efficiency of different sorbents to take up methylene blue, which is a widely used basic dye (Peterlin *et al.* 2009; Acemioğlu *et al.*

2010; Aksu *et al.* 2010). Though such studies have revealed many interesting details about the mechanism of dye uptake, the general consensus is that most ordinary cellulosic materials can be used effectively for the removal of basic dyes from aqueous solution. Though certain studies have demonstrated increased adsorption performance following physical or chemical modification of the biosorbent (Gong *et al.* 2006; Chadlia and Farouk 2007), the motivation for carrying out such modifications is not always clear.

Greater challenges can lie in the biosorption of negatively charged dye species onto cellulosic materials. Modifications have been shown to be effective for improving the uptake of selected anionic dyestuffs onto cellulose-based sorbents. These include cationization (El Ghali *et al.* 2010), or pyrolysis to make activated carbon sorbents (Thirumalisamy and Subbian 2010; Chowdhury *et al.* 2013). One way to account for the positive effects of carbonation on dye uptake is to note that such treatments generally increase the proportional aromatic content of the material and tend to make it more hydrophobic. Also, the very high and optimized levels of surface area and pore sizes in activated carbon products can lead to high adsorption capacity. Because many dye species of interact are much larger than heavy metal ionic species, it may be advantageous to adjust conditions of activation to yield larger pore sizes, *i.e.* more mesopores relative to micropores.

Oil Uptake and Effects of Cellulose Modifications

Oil spills are another major class of pollution that can be addressed, at least in part, by use of cellulose-based absorbent materials. Oils, as a matter of definition, are insoluble in water. A typical oil spill in water will include liquid oil, as well as possible oil-in-water emulsions, water-in-oil emulsions, and minor amounts of dissolved molecules (Hubbe *et al.* 2013). Here the main emphasis will be placed on removal of liquid oil from water.

Because of the relatively hydrophilic character of cellulosic materials, key challenges and opportunities can involve modifications to make the surfaces more hydrophobic. Increased uptake of liquid oil from water onto such hydrophobically modified sorbents has been shown (Sathasivam and Haris 2010; Gao *et al.* 2012; Payne *et al.* 2012). Alternatively, high performance also has been achieved with certain cellulosic materials that are naturally "waxy", meaning that they tend to shed water. Examples include kapok, milkweed seed hairs, and raw cotton fibers (Choi and Cloud 1992; Lim and Huang 2007). The feasibility of any hydrophobic treatment strategies to make cellulosic materials more suitable for oil sorption need to be weighed relative to these naturally hydrophobic materials. One also can consider the use of high-performing petrochemical-based sorbent materials, such as polypropylene fibers (Zahid *et al.* 1972; Wei *et al.* 2003).
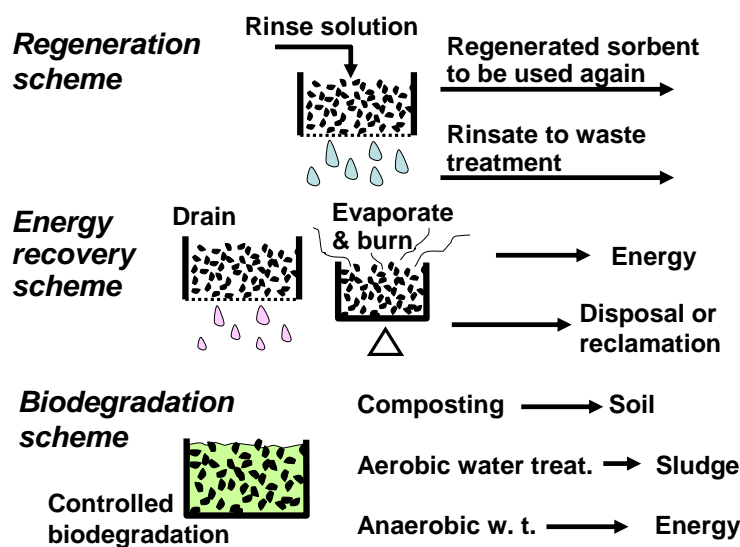
For use in water-free systems, the optimum surface character of an absorbent can follow completely different rules. A recent study (Payne *et al.* 2012) showed that hydrophobization of cellulose fibers can decrease the uptake of simulated crude oil in the absence of water. Because the surface free energy of most oils is low, they will spread spontaneously over higher-energy surfaces including those of cellulose-based materials. In such cases, efforts to decrease the surface energy of the substrate surfaces, making them more similar to that of the oil, may be unnecessary or even counterproductive.

In submerged systems, or when the sorbent material may be subjected to wave action, a hydrophobic character (or treatment) can render cellulose-based sorbents substantially more effective for the collection of oils (Payne *et al.* 2012). In addition to increasing the uptake of oil, the hydrophobic nature tends to hold onto bubbles, helping the material to float at the water surface (Korhonen *et al.* 2011; Likon *et al.* 2011). The possible sinking of sorbent material, either before it has become loaded with oil, is regarded as highly undesirable (Fingas 2011).

A particular challenge in the sorption of liquid or emulsified oils can involve a high viscosity of the pollutant. The high viscosity means that usually there will be little advantage to be gained by having a high fine-scale content of porosity. Rather, the best results are often achieved in such cases when using rather coarse, fibrous materials, in which the oil may be accommodated with relatively large spaces between fibers (Ribeiro *et al.* 2000). An exception to this rule is when one is interested in removing trace amounts of dissolved oily pollutants from water; in such cases high-area sorbents such as activated carbon, for instance, can be highly appropriate.

PROSPECTS FOR INTEGRATED APPROACHES TO BIOREMEDIATION

Looking towards the future, one can envision fully integrated biosorption systems in which potential pollutants are efficiently removed from both effluent streams and from the intake streams for potable water. The term "integrated" means that the removed materials are collected and put to their most valuable use and that net environmental impacts are minimized. The present section will focus on three such approaches and cite various publications that touch upon the relative value of each of these general strategies. Figure 3 shows schematic representations of the three main strategies to be considered.

Fig. 3. Schematic representations of three main strategies that could be used to deal with spent biosorbent material after its usage

Collect, Regenerate (and concentrate), Reuse

When an industrial material has been mixed with other materials and dispersed into water that gets passed on to the environment, then it can be regarded as a pollutant. But if the same material could be somehow concentrated and fractionated into its relatively pure components, then it might be considered as being a valuable commodity. It can be challenging, however, to put this principle into practice when dealing with contaminated water. First, individual pollutants dispersed or dissolved into water can have very low concentrations. It may be technologically challenging to come up with a method that can gather up enough of the material into a sufficiently concentrated form to have any commercial value. Furthermore, most polluted waters contain mixtures of contaminants; this means that efforts at collection and concentration can be expected to produce impure mixtures, which tend to have much lower value in comparison to pure substances.

The collection of heavy metal ions from heavily contaminated water may represent the best case scenario for efforts to reclaim a pollutant and isolate commercially valuable materials (Cui and Zhang 2008). The metals industry has expertise in concentrating and purifying various metals and related compounds (Tuncuk *et al.* 2012; Coman *et al.* 2013; Xei *et al.* 2013). Furthermore, the metal content within spent biosorbent material can be readily concentrated by the steps of drainage or pressing out the water, drying the spent sorbent material, and incineration to obtain mineral-rich ash (Gaballah and Kilbertus 1998). If each of the steps is done in an optimized manner, the final ash should contain most of the metals originally collected onto the sorbent. In principle, metals may be obtained by smelting or electrolytic reduction of oxides and other compounds in the ash (Agrawal *et al.* 2009; Sheoran *et al.* 2009; Coman *et al.* 2013). Methods of separation of mixtures of metals can be challenging, but at least the technologies are known.

As noted earlier, aqueous conditions can be adjusted such that classes of metal ions are released back into the water phase (Hubbe *et al.* 2011). The resulting regenerated sorbent material has been shown, in many cases, to be capable of adsorbing almost the same amount of the selected pollutant when used for a second, third, or additional time. This type of regeneration strategy seems especially appropriate for use in flow-through systems, making it possible to regenerate a packed bed without having to move the sorbent material (Chang 1997; Park *et al.* 2010). Ideally one can hope that the liquid mixture created during the regeneration process has a much lower volume in comparison to the effluent from which the heavy metal ions were initially collected. In other words, one hopes to achieve a relatively high concentration of the metal ions in the rinsate. Though many studies have specified conditions for effective regeneration (Hubbe *et al.* 2011), the concentration of metal ions in such rinsate has hardly been mentioned in such publications. Also, there has been almost no published comment about what to do next with such rinsate. In theory it would be possible to employ a variety of water treatment strategies to remove the metal ions from the water phase (Lester 1987). But if that is the objective, then one has to wonder what was the point of removing the metal species from the biosorbent in the previous step. It might make more sense to use an inexpensive sorbent material a single time and then landfill it, allowing the sorbent to continue its work of binding the metal species. More research is needed to

evaluate the long-term stability of such binding under the conditions of landfilling (Prechthai *et al.* 2008).

Dyes probably represent the worst-case scenario with respect to their collection from polluted water and subsequent re-use. The human eye can be extremely effective in discriminating minor differences in the coloration of manufactured objects. That means that any commercial dyestuffs need to be prepared in a highly reproducible way. The most successful strategies to redissolve dyes after their collection onto cellulosic material involve adjustments in pH (Jain *et al.* 2010; Hubbe *et al.* 2012). However, such approaches are typically only partially successful in releasing the dye into the solution phase, and the approach makes sense only in the case of dyes that are strongly acidic (to be released at high pH) or strongly basic (to be released at low pH). But that may be the easy part; there is no practical way to physically separate similar dyes of differing hue once they are present in the same aqueous mixture.

In the case of oils, one can envision a process analogous to dry cleaning in which oils are extracted from spent biosorbent. Conventional dry cleaning is a costly process, and additional costs would be added if efforts were made to remove the oil from the dry-cleaning fluid. Perhaps the most promising systems that involve reclamation of oils from sorbent materials are those that are incorporated into skimmer technology for collection of recently-spilled petroleum from the water surface (Fingas 2011; Hubbe *et al.* 2013). In such cases there can be sufficiently high amounts of oil that it can be squeezed from the sorbent material (Choi *et al.* 1993; Silva-Tilak 2002). After separation of the oil and water phases, the oil content may have commercial value.

Collect, Incinerate (and concentrate), Capture energy

Various researchers have considered strategies in which the energy content of biosorbent material is at least partly recovered after its usage (Chouchene *et al.* 2012; Vanem *et al.* 2008). Such approaches can be justified, in many cases, by the fact that a relatively large amount of absorbent material may have been used to collect minor amounts of highly objectionable metals, dyes, or organic toxins from water. So rather than to expect to recover value from the collected pollutants, one turns ones attention to recovering value from the used absorbent.

One of the biggest challenges to recovering energy content from biosorbent materials involves the water-soaked nature of many such materials. The energy required to remove such water by some combination or draining, squeezing, and evaporation (with emphasis on evaporation) has been considered in a few studies (Chouchene *et al.* 2012; Jeguirim *et al.* 2012). One possible approach, which may minimize the amount of fuel energy needed to dry biosorbent materials in preparation for their incineration, involves spreading out the material to dry in the sunlight (Chouchene *et al.* 2012). This might be an excellent approach for applications in hot, low-humidity climates, but perhaps not well suited for north Mediterranean regions for which it has been initially investigated. Another possible strategy would be to employ a multiple-effect evaporator system to minimize the amount of steam that is needed to concentrate the material and get it ready for final evaporation of the remaining water (Kumar *et al.* 2013). This type of system is widely used for recovery of chemicals used in the pulping of wood for use in paper manufacture.

A particular challenge of schemes relying upon incineration is the tendency of certain substances to either foul the incineration equipment or to raise the likelihood of gaseous or airborne particulate pollution problems. As a large and visible source of smoke and other toxic substances (Valerio 2010; Tsai and Wu 2013), incineration operations are likely targets of regulation, fines, and litigation. If a sorbent has been exposed to salt water during its use, perhaps due to collection of spilled oil from seawater, then the salt not only can be corrosive to process equipment but also can become part of the smoke (Viklund *et al.* 2013). Such problems can be overcome, for instance by use of scrubber technologies (Le Cloirec 2012), and by advanced metallurgy (Milos *et al.* 2012), but such fixes can be expensive.

Collect and Biodegrade

A third main approach to dealing with used biosorbent materials involves biodegradation. Though biodegradation can be regarded as being a natural process, the conditions can be set up in such a way as to speed up the process and to minimize the generation of unwanted gaseous species. Three major classes of such treatment are composting, conventional secondary treatment of wastewater, and anaerobic digestion. Though each of these kinds of treatment has been well studied, relatively little attention has been paid to their applications to consume or decontaminate spent biosorbent materials after their use.

Composting can be defined as a controlled process of aerobic decomposition of damp material in which conditions allow for a substantial rise in temperature, thus increasing the rate of biodegradation (Hubbe *et al.* 2010). By placing the degradable material in a sufficiently large pile, the heat generated by microbial metabolism can be sufficient to maintain the pile at temperatures that are ideal for various classes of microbes. Enzymes released by fungal and bacterial species naturally present in the materials can proliferate and help to break down the lignocellulosic matter. The goal of a typical composting operation is to (a) eliminate any toxic, odorous, or disease-generating substances, (b) reduce the amount of material, and (c) to end up with a humus-rich mixture that can enhance the fertility and water-holding ability of soil. In particular, break-down products of the slow-to-decompose lignin components of wood, *i.e.* the humus, is known to hold strongly to both water molecules and essential minerals (Selim and Zhang 2013).

The relationship between composting processes and polluting substances has attracted relatively little attention from researchers (Semple *et al.* 2001; Purnomo *et al.* 2011). Perhaps this is because the incorporation of serious pollutants into a composting process is viewed as being contrary to the goal of producing a high-quality amendment for healthy soil. Also, there may be reluctance among some technologists to seriously consider using a process that is more often associated with organic gardening. Since the humus within compost tends to resist further aerobic breakdown (Hubbe *et al.* 2010), one can expect it to remain in the soil (or landfill), binding heavy metals and/or hydrophobic materials, for many decades into the future. However, research to back up such expectations is needed. Key questions to be addressed in such research are as follows:

- Even before composting, is the pollutant already being held with sufficient permanency as to preclude significant toxic effects and to call into question the need for the proposed composting treatment?
- Can conventional composting processes reduce the toxic or other adverse environmental effects of the pollutants in addition to the known ability of composting to minimize present and future emission of greenhouse gases from the organic matter?
- Does the compost resulting from processing of spent biosorbent need to be excluded from certain uses, such as the conditioning of soils to be used for the growing of food crops?

Conventional secondary treatment of wastewater is similar to composting with respect to its reliance on aerobic microbes – as well as the enzymes released from the microbes – to break down various organic molecules. What is different is that everything takes place under water during secondary wastewater treatment. Some of the biological sludge that is generated during such processing, the so-called activated sludge, usually is recirculated to the next incoming batch of wastewater to be treated (Ni and Yu 2012). In that way the operators are able to inoculate each batch with a diverse population of bacteria and fungi, allowing for the efficient breakdown of such species as hemicellulose, starches, *etc.* But certain dye species are known to be resistant to biodegradation (Khan *et al.* 2013). In some cases it is this very resistance to biodegradation that has prompted technologists to consider biosorption in the first place. So it may in the end make more sense to carry out the conventional wastewater treatment first and then to employ biosorption as a follow-up, polishing treatment to reduce the remaining concentrations of dissolved pollutants to very low levels.

Anaerobic digestion is the other main strategy that needs to be considered seriously as a way of dealing with spent biosorbent. Such treatment can offer effective detoxification of many toxic organic compounds (van der Zee and Villaverde 2005; Hwang *et al.* 2007). By using anaerobic digestion it is also possible to collect flammable byproduct gases such as hydrogen and methane, which then can be used in place of fossil fuels. Such research could be extended to consider what happens when such pollutants are to be treated while they remain adsorbed on the surface of a biosorbent, upon which they have been collected. A question to figure out is whether the presence of cellulose-based material during anaerobic treatment might either promote or interfere with the desired chemical transformations.

CLOSING STATEMENTS

The adsorption of pollutants such as heavy metals, dyes, and spilled oils onto cellulose-based materials appears to be a promising approach with good prospects for more widespread usage in years ahead. But there are a great many questions that await the attention of researchers. In particular, more work is needed to determine the most appropriate way of dealing with such sorbent materials after the target pollutants have been removed from the water. Modification of cellulose-based materials appears to be an

effective strategy to improve their effectiveness for reducing water-borne pollutants to very low concentrations. Each such modification needs to be scrutinized relative to the net environmental impacts. Technologists and entrepreneurs need also to consider the possibility that certain as-received cellulosic materials often can outperform various other modified sorbents. In other cases, modest steps such as heat treatment or oxidation can have potential to yield large benefits in terms of pollution control that more than compensate for the environmental costs associated with the treatments themselves.

REFERENCES CITED

Acemioğlu, B., Kertmen, M., Diğrak, M., and Alma, M. H. (2010). "Use of *Aspergillus wentii* for biosorption of methylene blue from aqueous solution," *African J. Biotechnol*. 9(6), 874-881.

Agrawal, A., Kumar, V., and Pandey, B. D. (2006). "Remediation options for the treatment of electroplating and leather tanning effluent containing chromium - A review," *Mineral Processing Extrac. Metall. Rev*. 27(2), 99-130.

Agrawal, A., Kumari, S., and Sahu, K. K. (2009). "Iron and copper recovery/removal from industrial wastes: A review," *Indust. Eng. Chem. Res*. 48(13), 6145-6161.

Aguilera, F., Mendez, L., Pasaro, E., and Laffon, B. (2010). "Review of the effects of exposure to spilled oils on human health," *J. Appl. Toxicol*. 30(4), 291-301.

Ahluwalia, S. S., and Goyal, D. (2005). "Microbial and plant derived biomass for removal of heavy metals from waste water," *Bioresour. Technol*. 98, 2243-2257.

Aksu, Z., Açikel, U., Kabasakal, E., and Tezer, S. (2002). "Equilibrium modeling of individual and simultaneous biosorption of chromium(VI) and nickel(II) onto dried activated sludge," *Water Res*. 36(12), 3063-3073.

Aksu, Z., Acikel, U., and Kutsal, T. (1997). "Application of multicomponent adsorption isotherms to simultaneous biosorption of iron(III) and chromium(VI) on *C. vulgaris*," *J. Chem. Technol. Biotechnol*. 70(4), 368-378.

Aksu, Z., Ertugrul, S., and Donmez, G. (2010). "Methylene blue biosorption by *Rhizopus arrhizus*: Effect of SDS (sodium dodecylsulfate) surfactant on biosorption properties," *Chem. Eng. J*. 158(3), 474-481.

Aksu, Z., and Donmez, G. (2006). "Binary biosorption of cadmium(II) and nickel(II) onto dried *Chlorella vulgaris*: Co-ion effect on mono-component isotherm parameters," *Process Biochem*. 41(4), 860-868.

Al-Degs, Y. S., Khraisheh, M. A. M., Allen, S. J., Ahmad, M. N., and Walker, G. M. (2007). "Competitive adsorption of reactive dyes from solution: Equilibrium isotherm studies in single and multisolute systems," *Chem. Eng. J*. 128(2-3), 163-167.

Babel, S, and Kurniawan, T. A. (2004). "Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agent and/or chitosan," *Chemosphere* 54(7), 951-967.

Baillet, F., Magnin, J.-P., Cheruy, A., and Ozil, P. (1998). "Chromium precipitation by the acidophilic bacterium *Thiobacillus ferrooxidans*," *Biotechnology Letters* 20(1), 95-99.

Barakat, M. A. (2011). "New trends in removing heavy metals from industrial wastewater," *Arabian J. Chem.* 4(4), 361-377.

Bishnoi, N. R., and Garima. (2005). "Fungus - An alternative for bioremediation of heavy metal containing wastewater: A review," *J. Sci. Indus. Res*. 64(2), 93-100.

Carro, D., Delgado, J., Vazquez, A., Barrientos, V., and Juncosa, R. (2008). "Final disposal of the wastes associated with the oil spill of the tanker prestige through its stabilization with quicklime and granite fines," *Soil Sediment Contam*. 17(4), 393-410.

Chadlia, A., and Farouk, M. M. (2007). "Removal of basic blue 41 from aqueous solution by carboxymethylated *Posidonia oceanica*," *J. Appl. Poly. Sci*. 103(2), 1215-1225.

Chadlia, A., Mohamed, K., Najah, L., and Farouk, M. M. (2009). "Preparation and characterization of new succinic anhydride grafted *Posidonia* for the removal of organic and inorganic pollutants," *J. Hazardous Mater*. 172(2-3), 1579-1590.

Chang, J. S., Law, R., and Chang, C. C. (1997). "Biosorption of lead, copper and cadmium by biomass of *Pseudomonas aeruginosa* PU21," *Water Research* 31(7), 1651-1658.

Chen, T. Y., Chiu, M. S., and Weng, C.-N. (2006). "Derivation of the generalized Young-Laplace equation of curved interfaces in nanoscaled solids," *J. Appl. Physics* 100(7), article. No. 074308.

Chew, J. J., and Doshi, V. (2011). "Recent advances in biomass pretreatment – Torrefaction fundamentals and technology," *Renewable and Sustainable Energy Reviews* 15(8), 4212-4222.

Choi, H.-M., and Cloud, R. M. (1992). "Natural sorbents in oil spill cleanup," *Environ. Sci. Technol*. 26(4), 772-776.

Choi, H.-M., Kwon, H.-J., and Moreau, J. P. (1993). "Cotton nonwovens as oil spill cleanup sorbents," *Textile Res. J*. 63, 211-218.

Chouchene, A., Jeguirim, M., Trouve, G., Favre-Reguillon, A., and Le Buzit, G. (2010). "Combined process for the treatment of olive oil mill wastewater: Absorption on sawdust and combustion of the impregnated sawdust," *Bioresour. Technol*. 101(18), 6962-6971.

Chowdhury, Z. Z., Abd Hamid, S. B., Das, R., Hassan, M. R., Zain, S. M., Khalid, K., and Uddin, M. N. (2013). "Preparation of carbonaceous adsorbents from lignocellulosic biomass and their use in removal of contaminants from aqueous solution," *BioResources* 8(4), 6523-6555.

Coman, V., Robotin, B., and Ilea, P. (2013). "Nickel recovery/removal from industrial wastes: A review," *Resources Conserv. Recyc*. 73, 229-238.

Cui, J. R., and Zhang, L. F. (2008). "Metallurgical recovery of metals from electronic waste: A review," *J. Hazardous Mater*. 158(2-3), 228-256.

da Silva, L. G., Ruggiero, R., Gontijo, P. D, Pinto, R. B., Royer, B., Lima, E. C., Fernandes, T. H. M., and Calvete, T. (2011). "Adsorption of Brilliant Red 2BE dye from water solutions by a chemically modified sugarcane bagasse lignin," *Chem. Eng. J*. 168, 620-628.

De Hoces, M. C., Vicente, I. D. A., Rico, I. L. R., Falcon, M. F. C., and Martin-Lara, M. A. (2011). "Life cycle assessment on producing a heavy metals biosorbent from sugarcane bagasse," *Desalination and Water Treatment* 30, 272-277.

DeLaune, R. D., Wright, A. L. (2011). "Projected impact of Deepwater Horizon oil spill on US Gulf Coast wetlands," *Soil Sci. Soc. Amer. J.* 75(5), 1602-1612.

Demirbas, A. (2008). "Heavy metal adsorption onto agro-based waste materials: A review," *J. Hazardous Mater.* 157(2-3), 220-229.

Dias, J. M., Alvim-Ferraz, M. C. M., Almeida, M. F., Rivera-Utrilla, J., and Sanchez-Polo, M. (2007). "Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review," *J. Environ. Manag.* 85(4), 833-846.

Dundar, T., Buyuksari, U., Avci, E., and Akkilic, H. (2012). "Effect of heat treatment on the physical and mechanical properties of compression and opposite wood of black pine," *BioResources* 7(4), 5009-5018.

El Ghali, A., Baouab, M. H. V., and Roudesli, M. S. (2010). "*Stipa tenacessima* L cationized fibers as adsorbent of anionic dyes," *J. Appl. Polymer Sci.* 116(6), 3148-3161.

EPA (2013). "Greenhouse gas equivalencies calculator," http://www.epa.gov/cleanenergy/energy-resources/calculator.html

Fingas, M. (2011). *Oil Spill Science and Technology*, Elsevier, Amsterdam.

Foglarova, M., Prokop, J., and Milichovsky, M. (2009). "Oxidized cellulose: An application in the form of sorption filter materials," *J. Appl. Polymer Sci.* 112(2), 669-678.

Freundlich, H. M. F. (1907). "Über die Adsorption in Lösungen," *Zeitschrift fur Physikalische Chemie* (Leipzig). A 57, 385-470.

Fu, F. L., and Wang, Q. (2011). "Removal of heavy metal ions from wastewater: A review," *J. Environ. Manag.* 92(3), 407-418.

Gaballah, I., and Kilbertus, G. (1998). "Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks," *Journal of Geochemical Exploration* 62(1-3), 241-286.

Gadd, G. M. (2009). "Biosorption: Critical review of scientific rationale, environmental importance and significance for pollution treatment," *J. Chem. Technol. Biotech.* 84(1), 13-28.

Gao, Y., Zhou, Y. T., Zhang, X. L., Zhang, L. P., and Qu, P. (2012). "Synthesis and characteristics of graft copolymers of poly(butyl acrylate) and cellulose fiber with ultrasonic processing as a material for oil absorption," *BioResources* 7(1), 135-147.

Gong, R., Jin, Y., Chen, F., and Chen, J. (2006). "Enhanced malachite green removal from aqueous solution by citric acid modified rice straw," *J. Hazard Mater. B* 137, 865-870.

Gupta, V. K., Mohan, D., Sharma, S., and Park, K. T. (1999). "Removal of chromium (VI) from electroplating industry wastewater using bagasse fly ash – A sugar industry waste material," *The Environmentalist* 19, 129-136.

Gyurcsik, B., and Nagy, L. (2000). "Carbohydrates as ligands: Coordination equilibria and structure of the metal complexes," *Coordination Chem. Rev.* 203, 81-149.

Ho, Y. S., and McKay, G. (1999). "Competitive sorption of copper and nickel ions from aqueous solution using peat," *Adsorption* 5(4), 409-417.

Ho, Y. S., Ng, J. C. Y., and McKay, G. (2000b). "Kinetics of pollutant sorption by biosorbents: Review," *Separ. Purif. Methods* 29(2), 189-232.

Hubbe, M. A., Beck, K. R., O'Neal, W. G., and Sharma, Y. C. (2012). "Cellulosic substrates for removal of pollutants from aqueous systems: A review. 2. Dyes," *BioResources* 7(2), 2592-2687.

Hubbe, M. A., Hasan, S. H., and Ducoste, J. J. (2011). "Cellulosic substrates for removal of pollutants from aqueous systems: A review. 1. Metals," *BioResources* 6(2), 2161-2287.

Hubbe, M. A., Nazhad, M., and Sánchez, C. (2010). "Composting as a way to convert cellulosic biomass and organic waste into high-value soil amendments: A review," *BioResources* 5(4), 2808-2854.

Hubbe, M. A., Rojas, O. J., Fingas, M., and Gupta, B. S. (2013). "Cellulosic substrates for removal of pollutants from aqueous systems: A Review. 3. Spilled oil and emulsified organic liquids," *BioResources* 8(2), 3038-3097.

Hunger, K. (ed.) (2003), *Industrial Dyes: Chemistry, Properties, Applications*, Wiley-VCH, Weinheim, Germany.

Hwang, H.-M., Hu, X., and Zhao, X. (2007). "Enhanced bioremendiation of polycyclic aromatic hydrocarbons by environmentally friendly techniques," *J. Environ. Sci. Health. Pt. C – Enviorn. Carcinogen. Ecottox. Revs*. 25(4), 313-352.

Jain, S., and Jayaram, R. V. (2010). "Removal of basic dyes from aqueous solution by low-cost adsorbent: Wood apple shell (*Feronia acidissima*)," *Desalination* 250(3), 921-927.

Jeguirim, M., Chouchène, A., Réguillon, A. F., Trouvé, G., and Le Buzit, G. (2012). "A new valorisation strategy of olive mill wastewater: Impregnation on sawdust and combustion," *Resources, Conservation and Recycling* 59, 4-8.

Karnitz, O., Gurgel, L. V. A., and Gil, L. F. (2010). "Removal of Ca(II) and Mg(II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse grafted with EDTA dianhydride (EDTAD)," *Carbohydrate Polymers* 79(1), 184-191.

Khan, R., Bhawana, P., and Fulekar, M. H. (2013). "Microbial decolorization and degradation of synthetic dyes: A review," *Revs. Environ. Sci. Biotech*. 12(1), 75-97.

Klasson, K. T., Wartelle, L. H., Rodgers, J. E., and Lima, I. M. (2009). "Copper(II) adsorption by activated carbons from pecan shells: Effect of oxygen level during activation," *Indus. Crops Prod*. 30(1), 72-77.

Korhonen, J. T., Kettunen, M., Ras, R. H. A., and Ikkala, O. (2011). "Hydrophobic nanocellulose aerogels as floating, sustainable, reusable, and recyclable oil absorbents," *ACS Appl. Mater. Interfaces* 3(6), 1813-1816.

Kriaa, A., Hamdi, N., and Srasra, E. (2011). "Adsorption studies of Methylene Blue dye on Tunisian activated lignin," *Russian J. Phys. Chem. A* 82(2), 279-287.

Kumar, D., Kumar, V., and Singh, V. P. (2013). "Modeling and dynamic simulation of mixed feed multi-effect evaporators in paper industry," *Appl. Math. Modelling* 37, 384-397.

Kumar, S. (2011). "Composting of municipal solid waste," *Critical Rev. Biotechnol*. 31(2), 112-136.

Kutnar, A., Kricej, B., Pavlic, M., and Petric, M. (2013). "Influence of treatment temperature on wettability of Norway spruce thermally modified in vacuum," *J. Adhes. Sci. Technol*. 27(9), 963-972.

Lagergren, S. (1898). "About the theory of so-called adsorption of soluble substances," *K. Sven. Vetenskapsakad. Handl*. 24, 1-39.

Langmuir, I. (1918). "The adsorption of gases on plane surface of glass, mica and platinum," *J. Am. Chem. Soc*. 40, 1361-1403.

Lebek, J., and Wardas, W. (1996). "Adsorption of some textile dyes on post-vanillin lignin during its precipitation," *Cellulose Chem. Technol*. 30(3-4), 213-221.

Le Cloirec, P. (2012). "Treatments of polluted emissions from incinerator gases: A succinct review," *Revs. Environ. Sci. Biotech*. 11(4), 381-392.

Lester, J. N. (1987). *Heavy Metals in Wastewater and Sludge Treatments Processes*, (ed.), CRC Press, Boca Raton, FL.

Leyva-Ramos, R., Bernal-Jacome, L. A., Guerrero-Coronado, R. M., and Fuentes-Rubio, L. (2001). "Competitive adsorption of Cd(II) and Zn(II) from aqueous solution onto activated carbon," *Separ. Sci. Technol*. 36(16), 3673-3687.

Li, X. Y., Zhang, L. W., and Wang, C. W. (2012). "Review of disposal of concentrate streams from nanofiltration (NF) or reverse osmosis (RO) membrane process," *Adv. Environ. Sci. Eng.*, book ser. *Advanced Materials Research*, 518-523, 3470-3475.

Likon, M., Cernec, F., Svegl, F., Saarela, J., and Zimmie, T. F. (2011). "Papermill industrial waste as a sustainable source for high efficiency absorbent production," *Waste Manag*. 31(6), 1350-1356.

Lim, T. T., and Huang, X. F. (2007). "Evaluation of kapok (*Ceiba pentandra* (L.) Gaertn.) as a natural hollow hydrophobic-oleophilic fibrous sorbent for oil spill cleanup," *Chemosphere* 66(5), 955-963.

Loukidou, M. X., Karapantsios, T. D., Zouboulis, A. I., and Matis, K. A. (2004). "Diffusion kinetic study of cadmium (II) biosorption by *Aeromonas caviae*," *J. Chem. Technol. Biotechnol.* 79(7), 711-719.

Lusth, H., Gradin, P. A., and Hellstrom, L. M. (2013). "A theoretical model of the prediction of energy consumption during the chipper canter process," *Nordic Pulp Paper Res. J.* 28(2), 211-215.

Lyubchik, S. I., Lyubchik, A. I., Galushko, O. L., Tikhonova, L. P., Vital, J., Fonseca, I. M., and Lyubchik, S. B. (2004). "Kinetics and thermodynamics of the Cr(III) adsorption on the activated carbon from co-mingled wastes," *Colloids Surf. A – Physicochem. Eng. Aspects* 242(1-3), 151-158.

Malkoc, E., and Nuhoglu, Y. (2007). "Potential of tea factory waste for chromium(VI) removal from aqueous solutions: Thermodynamic and kinetic studies," *Separ. Purif. Technol.* 54(3), 291-298.

Malkoc, E., Nuhoglu, Y., and Abali, Y. (2006a). "Cr(VI) adsorption by waste acorn of *Quercus ithaburensis* in fixed beds: Prediction of breakthrough curves," *Chem. Eng. J.* 119(1), 61-68.

Martínez, M., Miralles, N., Hidalgo, S., Fiol, N., Villaescusa, I., and Poch, J. (2006a). "Removal of lead(II) and cadmium(II) from aqueous solutions using grape stalk waste," *J. Hazard. Mater. B* 133, 203-211.

McKay, G., and Ho, Y. S. (1999). "Pseudo-second order model for sorption processes," *Process. Biochem.* 34, 451-465.

Milos, L., Salai, M., and Pacurar, C. (2012). "Behaviour of performance materials at corrosion media from the burning wastes," *Revista de Chimie* 63(11), 1172-1175 (2012).

Mohan, D., and Pittman, C. U. (2006). "Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water," *J. Hazardous Mater.* 137(2), 762-811.

Ni, B. J., and Yu, H.-Q. (2012). "Microbial products of activated sludge in biological wastewater treatment systems: A critical review," *Crit. Revs. Environ. Sci. Technol.* 42(2), 187-223.

O'Connell, D. W., Birkinshaw, C., and O'Dwyer, T. F. (2008). "Heavy metal adsorbents prepared from the modification of cellulose: A review," *Bioresour. Technol.* 99(15), 6709-6724.

Padgett, J. M. (2009). "Biodegradability of wood products under simulated landfill conditions," PhD Thesis, North Carolina State University.

Page, D. (1993). "A quantitative theory of the strength of wet webs," *J. Pulp Paper Sci.* 19(4), J175-J176.

Park, D., Lim, S.-R., Yun, Y.-S., and Park, J. M. (2008a). "Development of new Cr(VI)-biosorbent from agricultural biowaste," *Bioresour. Technol.* 99(18), 8810-8818.

Park, D., Yun, Y. S., Kim, J. Y., and Park, J. M. (2008b). "How to study Cr(VI) biosorption: Use of fermentation waste for detoxifying Cr(VI) in aqueous solution," *Chem. Eng. J.* 136(2-3), 173-179.

Park, D., Yun, Y. S., and Park, J. M. (2010). "The past, present, and future trends of biosorption," *Biotechnol. Bioproc. Eng.* 15(1), 86-102.

Payne, K. C., Jackson, C. D., Aizpurua, C. E., Rojas, O. J., and Hubbe, M. A. (2012). "Oil spills abatement: Factors affecting oil uptake by cellulosic fibers," *Environ. Sci. Technol.* 46(14), 7725-7730.

Peterlin, S., Drnovsek, T., Perdih, A., and Dolenc, D. (2009). "Dyeing of papermaking fibers with dyes of various structural types as a means for fiber characterization," *Acta Chimica Slovenica* 56(2), 418-425.

Plappally, A. K., and Lienhard, J. H. (2012). "Energy requirements for water production, treatment, end use, reclamation, and disposal," *Renewable & Sustainable Energy Reviews* 16(7), 4818-4848.

Porter, J. J. (1993). "Applied dyeing theory - Interpretation of sorption isotherms for mixtures of direct dyes on cellulose," *Textile Chemist and Colorist* 25(2), 27-37.

Prechthai, T., Parkpian, P., and Visvanathan, C. (2008). "Assessment of heavy metal contamination and its mobilization from municipal solid waste open dumping site," *J. Hazard. Mater.* 156, 86-94.

Purnomo, A. S., Mori, T., Kamei, I., and Kondo, R. (2011). "Basic studies and applications on bioremediation of DTT: A review," *Intl. Biodeter. Biodegrad.* 65(7), 921-930.

Rai, H. S., Bhattacharyya, M. S., Singh, J., Bansal, T. K., Vats, P., and Banerjee, U. C. (2005). "Removal of dyes from the effluent of textile and dyestuff manufacturing industry: A review of emerging techniques with references to biological treatment," *Crit. Rev. Environ. Sci. Technol.* 35(3), 219-238.

Rao, R. A. K., Rehman, F., and Kashifuddin, M. (2012). "Removal of Cr(VI) from electroplating wastewater using fruit peel of Leechi (*Litchi chenensis*)," *Desalination and Water Treatment* 49, 136-146.

Ribeiro, T. M. H., Smith, R. W. and Rubio, J. (2000). "Sorption of oils by nonliving biomass of a *Salvinia* sp.," *Environ. Sci. Technol.* 34(24), 5201-5205.

Sathasivam, K., and Haris, M. R. H. M. (2010). "Adsorption kinetics and capacity of fatty acid-modified banana trunk fibers for oil in water," *Water Air Soil Pollution* 213(1-4), 413-423.

Selim, H. M., and Zhang, H. (2013). "Modeling approaches of competitive sorption and transport of trace metals and metalloids in soils: A review," *J. Environ. Qual.* 42(3), 640-653.

Semple, K. T., Reid, B. J., and Fermor, T. R. (2001). "Impact of composting strategies on the treatment of soils contaminated with organic pollutants," *Environ. Pollut.* 112(2), 269-283.

Sheng, P. X., Ting, Y. P., and Chen, J. P. (2007). "Biosorption of heavy metal ions (Pb, Cu, and Cd) from aqueous solutions by the marine alga *Sargassum* sp. in single- and multiple-metal systems," *Indus. Eng. Chem. Res.* 46(8), 2438-2444.

Sheoran, V., Sheoran, A. S., and Poonia, P. (2009). "Phytomining: A review," *Minerals Eng.* 22(12), 1007-1019.

Shoemaker, J. K., and Schrag, D. P. (2013). "The danger of overvaluing methane's influence on future climate change," *Climate Change* 120, 903-914.

Silva-Tilak, V. (2002). "Method of oil cleanup using coconut coir pitch," US Pat. 6,391,120.

Srivastava, V. C., Mall, I. D., and Mishra, I. M. (2006b). "Modelling individual and competitive adsorption of cadmium(II) and zinc(II) metal ions from aqueous solution onto bagasse fly ash," *Separ. Sci. Technol.* 41(12), 2685-2710.

Stelte, W., Sanadi, A. R., Shang, L., Holm, J. K., Ahrenfeldt, J., and Henriksen, U. B. (2012). "Recent developments in biomass pelletization – A review," *BioResources* 7(3), 4451-4490.

Stone, J. E., and Scallan, A. M. (1966). "Influence of drying on the pore structures of the cell wall," in: *Consolidation of the Paper Web*, Trans. Symp. Cambridge, Sept. 1965, F. Bolam (ed.), Tech. Sec. British Paper and Board Makers' Assoc. Inc, London, Vol. 1, 145-174.

Stratton, R. A., and Colson, N. L. (1993). "Fiber wall damage during bond failure," *Nordic Pulp Paper Res. J.* 8(2), 245-249, 257.

Sun, P., Shang, Z. X., Gai, G. S., Wu, C. B., and Yang, Y. F. (2012). "Research on pulverizing characteristic of woody biomass by cutting mill," *Powder Technol. Appl. IV*, in book ser. *Advanced Materials Research* 454, 261-267.

Svecova, L., Spanelova, M., Kubal, M., and Guibal, E. (2006). "Cadmium, lead and mercury biosorption on waste fungal biomass issued from fermentation industry. 1. Equilibrium studies," *Sep. Purif. Technol.* 52(1), 142-153.

Thirumalisamy, S., and Subbian, M. (2010). "Removal of methylene blue from aqueous solution by activated carbon prepared from the peel of *Cucumis sativa* fruit by adsorption," *BioResources* 5(1), 419-437.

Tsai, W.-T., and Wu, P.-H. (2013). "Environmental concerns about carcinogenic air toxics produced from waste woods as alternative energy sources," *Energy Sources. Pt. A – Recov. Util. Environ. Effects* 35(8), 725-732.

Tuncuk, A., Stazi, V., Akcil, A., Yazici, E. Y., and Deveci, H. (2102). "Aqueous metal recovery techniques from e-scrap: Hydrometallurgy in recycling," *Minerals Eng.* 25(1), 28-37.

Valerio, F. (2010). "Environmental impacts of post-consumer material managements: Recycling, biological treatments, incineration," *Waste Manag.* 30(11), 2354-2361.

Van der Zee and Villaverde, S. (2005). "Combined anaerobic-aerobic treatment of azo dyes – A short review of bioreactor studies," *Water Res.* 39(8), 1425-1440.

Vanem, E., Endresen, O., and Skjong, R. (2008). "Cost-effectiveness criteria for marine oil spill preventive measures," *Reliability Eng. Sys. Safety* 93(9), 1354-1368.

Vijayaraghavan, K., Lee, M. W., and Yun, Y. S. (2008). "Evaluation of fermentation waste (*Corynebacterium glutamicum*) as a biosorbent for the treatment of nickel(II)-bearing solutions," *Biochem. Eng. J.* 41(3), 228-233.

Viklund, P., Hjornhede, A., Henderson, P., Stalenheim, A., and Petterson, R. (2013). "Corrosion of superheater materials in waste-to-energy plant," *Fuel Process. Technol.* 105, 106-112.

Weber, W. J., and Morris, J. C. (1963). "Equilibrium and capacities for adsorption on carbon," *J. Sanit. Eng. Div. ASCE* 89, 31-59.

Wei, Q. F., Mather, R. R., Fotheringham, A. R., and Yang, R. D. (2003). "Evaluation of nonwoven polypropylene oil sorbents in marine oil-spill recovery," *Marine Pollution Bulletin* 46, 780-783.

Xie, J. Z., Chang, H. L., and Kilbane, J. J. (1996). "Removal and recovery of metal ions from wastewater using biosorbents and chemically modified biosorbents," *Bioresour. Technol.* 57(2), 127-136.

Xei, F., Dreisinger, D., and Doyle, F. (2013). "A review of recovery of copper and cyanide from waste cyanide solutions," *Mineral Processing and Extractive Metallurgy Review* 34(6), 387-411.

Xiu, G. H., and Li, P. (2000). "Prediction of breakthrough curves for adsorption of lead(II) on activated carbon fibers in a fixed bed," *Carbon* 38(7), 975-981.

Zahid, M. A., Halligan, J. E., and Johnson, R. F. (1972). "Oil slick removal using matrices of polypropylene filaments," *Indust. Eng. Chem. Process Des. Dev.* 11(4), 550-558.