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Biosorption of Heavy Metals by Lignocellulosic Biomass and Chemical Analysis

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Many types of lignocellulosic biomass show effective binding of toxic heavy metals from industrial and environmental effluents. Biosorption is an emerging option for conventional methods to remove heavy metals, some of them with even better efficiencies compared to conventional methods. Raw material for biosorption is typically low-cost and easily available, including agricultural waste or forest residues such as sawdust, bark, or needles. This review concentrates on the accumulation of heavy metals by lignocellulosic biosorbents. Thus far, biosorption has not been economically feasible on a large scale and needs further development for profitability. Industrial-scale wood-based biosorbent applications are especially still lacking. Moreover, due to legislative demands, there is an increasing need for accurate and reliable analytical methods for metal analysis of environmental and industrial effluents. In the future, biosorption processes are likely to become common, and the requirement for environmental monitoring will increase due to ever restricting regulations. This emphasizes not only the need for the development of feasible process solutions, but also a requirement for accurate analytical methods.

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INTRODUCTION

In industrialized countries, biomass contributes to approximately 10 to 15% of energy demand, while nuclear and fossil fuels cover the remaining percentage (Khan *et al*. 2009). In developing countries, biomass consumption can account for up to one third of total energy supplies (Faaij 2004). In the European Union (EU), the utilization of biomass has increased in recent decades and is expected to increase further in the future (Nakicenovic and Swart 2000). In the EU, the target has been set by the Renewable Energy Directive to reach a target of 20% final energy consumption from renewable sources by the year 2020. The member states have committed to reaching their own national renewables targets, ranging from 10% in Malta to 49% in Sweden (EC 2009).

Lignocellulosic biomass refers to plant material composed of cellulose, hemicellulose, lignin, and extractives. Extractives can be defined as a group of hydrophilic and hydrophobic, organic and inorganic components in wood other than cellulose, hemicellulose, and lignin. Lignocellulosic biomass can be classified into virgin and waste biomass, including wood-based biomass. Wood biomass is harvested for industrial purposes and often is available in large quantities at an economical price. In this context, wood biomass is defined as biomass derived from lignified plants, such as trees, bushes, and forest residues.

Metals and chemicals used in industrial processes have led to the generation of large volumes of effluents with toxic heavy metals, for example, in mining, mineral processing, and metallurgical operations. Metals are categorized as biologically essential and non-essential, the latter including aluminum (Al), cadmium (Cd), mercury (Hg), tin (Sn), and lead (Pb), which have no known biological function but increasing toxicity at elevated concentrations (Sfakianakis *et al.* 2011). Essential metals, such as copper (Cu), chromium (Cr), cobalt (Co), iron (Fe), molybdenum (Mo), nickel (Ni), and zinc (Zn) play a biological role, showing either metabolic deficiencies or toxic effects at increased concentrations. Heavy metals are recalcitrant elements and can pollute water resources or accumulate and concentrate in living tissue (Mata *et al*. 2009). Heavy metals can enter the human diet and accumulate gradually in the human body. Depending on the element and the length of exposure, a variety of adverse health effects can occur, such as learning difficulties (Pb), neurological and psychological symptoms (Hg), nephrotoxicity, osteotoxicity, kidney damage (Cd), lung damage (Hg), negative gastrointestinal and central nervous symptoms (arsenic, As), and the increased risk of cancer (WHO 1992; Järup 2003; Li *et al*. 2006).

Heavy metal contamination is a serious concern in many countries (Mahar *et al*. 2016). For example, Cd pollution has become one of the most serious environmental problems worldwide (Folgar *et al*. 2009; Zacchini *et al*. 2009). Conventional treatment technologies are not economical and can generate large amounts of toxic sludge (Ahluwalia and Goyal 2007).

There is an urgent need to develop more cost-effective methods due to the high costs of traditional methods used to remove heavy metals from wastewaters. Sorption of metals by wood-based biomass has large potential in removing metals from aqueous solutions and their recovery for further use. Treetops and branches make up 20 to 30% of the aboveground biomass of trees, which provides a large potential quantity of material suitable for such a purpose (Werkelin *et al.* 2010).

This review aims at presenting suitable methods for the removal of heavy metals from aqueous environmental and industrial effluents. Although there are a variety of living (bacteria, molds, and fungi) and non-living (industrial and agricultural waste, forest residues) materials suitable for biosorption, the authors concentrated on the biosorption of wood-based biomass.

Expectedly, the use of biomass for a variety of forestry and wood-based industrial purposes on a commercial and municipal scale will become more common, as well as achieving policy goals on renewable energy. However, biosorption has not yet been cost-effective on a large scale, which limits its use in commercial applications (Crini 2006). This leads to the requirement of a variety of statutory follow-ups of chemicals and heavy metals. In the EU, the treatment of wastewater and sludge are controlled by the European Commission Urban Waste Water Directive 91/271/EEC (EC 1991). This regulation contains limits for metal content in reused sewage sludge. Additionally, the United States Environmental Protection Agency (EPA) has listed the maximum allowable limits for several heavy metals. For this purpose, standardized analytical methods are required to detect and quantify heavy metal concentrations. Therefore, a variety of analytical methods to detect and quantify heavy metals was reviewed.

INORGANICS IN BIOMASS

Metals in Biomass

The elemental composition of dry wood is typically approximately 50% carbon, 6% hydrogen, 44% oxygen, and trace amounts of inorganic compounds, varying based on wood species and the place of growth. Typically, coniferous species (softwood) have a higher cellulose and lignin content and a lower pentosane content compared to deciduous (hardwood) species. Additionally, ash content, the quantity of inorganics in wood, is often higher in hardwoods (Pettersen 1984; Rowell *et al.* 2013). In total, the proportion of inorganics ranges from 0.5 to 1%, and rarely exceeds 1% of dry wood in temperate zones (Sjöström and Alén 1998). However, wood in a tropical or subtropical region can contain inorganics of up to 5%.

Among the inorganics in wood, calcium (Ca), magnesium (Mg), and potassium (K) are the most common, comprising up to 80% of the inorganic material, wood ash being mainly Ca carbonate due to the high Ca content of wood material (Lambert 1981; Khan *et al*. 2009). There are also trace amounts of heavy metals, such as Al, barium (Ba), boron (B), Co, Cr, Cu, Fe, gallium (Ga), lithium (Li), manganese (Mn), Mo, Ni, Pb, rubidium (Rb), silicon (Si), silver (Ag), sodium (Na), strontium (Sr), titanium (Ti), Sn, vanadium (V), and Zn (Ellis 1965), some of them being essential for wood growth. In wood, they exist mostly as carbonates, sulfates, and oxalates or are bound to carboxyl groups of pectic materials (Hon and Shiraishi 1991). In biomass, sulfur (S) occurs in salts or as reduced in organic compounds, while chlorine (Cl) is mostly in soluble salts (Bryers 1996). In contrast, phosphorous (P) is in inorganic salts or organic compounds as esters and pyrophosphates, while silicon is mostly present as silica. Metal ions occur organically associated with biomass fibers or can remain in minerals precipitated as salts or occur in solution as free ions or complexes (Werkelin *et al.* 2010).

Environmental conditions, atmospheric pollutants, soil chemistry, and abiotic factors influence the tree growth, chemical composition, and location of inorganics within the tree (Jyske *et al*. 2014). For example, trees with compression wood show different elemental concentrations compared to unstressed wood (Prohaska *et al*. 1998). Chemical elements in annually formed tree rings are controlled by the cation-binding capacity of wood, radial growth rates, transformation of sapwood into heartwood, and radial translocation of elements in the tree stem. Most trees show declining cation concentration with increasing tree age due to binding-exchange properties in wood tissue as opposed to sap-soil chemistry. Due to translocation, the presence of an element in a specific year ring does not necessarily mean the presence of the element in the environment that year. This especially applies to young trees with no distinct heartwood formation (DeWalle *et al*. 1995).

There is an uneven distribution of inorganics in pine trees throughout wood tissues, needles, and bark. Cambium, the metabolically active boundary between sapwood and bark, can contain an order of magnitude of higher concentrations of Mg, Ca, K, and P compared to sapwood, while the lowest levels were found in heartwood (Yoshida *et al*. 2011). Werkelin *et al*. (2010) found higher levels of Cl in the shoots and needles of spruce compared to wood, twigs, and bark. Świetlik *et al*. (2012) studied the chemical distribution of Cd, Cu, Mn, Pb, and Zn in wood fly ash from pine sawdust and hardwood logs (acacia, alder, beech, birch, and oak). They found a higher proportion of heavy metals in hardwood than in softwood. Cd and Zn, which are regarded as

bioavailable, pose the highest potential hazard for the environment and human health (Świetlik *et al*. 2012).

Inorganic compounds are transferred into the wood *via* the roots. There is a high variability between species and especially between the barks of different species (Lambert 1981). Typically, the content of inorganics is higher in the needles, leaves, and bark compared to the stem wood (Harder and Einspehr 1980). The lowest contents of inorganics have been detected in the heartwood, with the lowest variability in the heartwood of different species. In earlywood, higher contents have been found compared to latewood (Rowell *et al*. 2013). Based on Pettersen (1984), the highest levels of inorganic compounds in different wood species were found in the basswood *Tilia americana* (K, 2.8 parts per thousand (ppt)), in quaking aspen *Populus tremuloides* (Ca 1.1 ppt, K 1.2 ppt), and in white ash *Fraxinus americana* (K 2.6 ppt, Mg 1.8 ppt).

Heavy Metals

Generally, the term heavy metal refers to metals or metalloids having an atomic density of more than 4 g dm^{-3} or 5 times that of water (Hawkes 1997) that are toxic or poisonous even at low concentrations (Nagajyoti *et al*. 2010). Heavy metals include, Ag, As, Cd, Co, Cr, Fe, Ni, Pb, Zn, and the platinum group elements. Heavy metals are also called trace elements due to their presence in trace (10 mg kg^{-1}) or ultratrace (1 µg kg^{-1}) quantities. From the ecotoxicological perspective, the most dangerous metals are Pb, Cd, Cr(VI), and Hg (Ahluwalia and Goyal 2007). Heavy metals found in aquatic environments have been a concern for decades (Bengtsson *et al*. 1979). Heavy metals are considered bioavailable in both organic and dissolved ionic forms.

Pollution due to heavy metals originates both from natural and anthropogenic sources. Naturally, heavy metals occur in ore minerals in the earth's crust and are released due to weathering, leading to a range of normal background concentrations in soil, sediments, water, and organisms (O'Connell *et al*. 2008). Among sedimentary rocks, shale has the highest concentrations of heavy metals, followed by limestone and sand-stone. Volcanoes, wind dust from desert regions, forest fires, and marine aerosols all contribute to the transporting of heavy metals (Nagajyoti *et al*. 2010). Industrial processes and other human activities have led to the contamination of soils with heavy metals (Laureysens *et al*. 2004). Heavy metals are introduced into the aquatic environment *via* industrial activities, such as from ore refining, tanneries, paper industry waste, and as pesticides (Celik and Demirbaş 2005). For example, mining, smelting, and agriculture have contaminated large areas with heavy metals, mostly with Cd, Cu, and Zn (Herawati *et al.* 2000).

Exposure to heavy metals has been linked to various cancers, kidney damage, autoimmunity, developmental retardation, and even death (Hokkanen *et al*. 2013). Additionally, Cr, Fe, selenium (Se), V, Cu, Ni, Cd, Hg, As, Zn, and Pb have known toxic effects and are hazardous to human health. For example, an accumulation of Cd in a human affects the kidneys and bones, and causes cancer, while Cr compounds are nephrotoxic and carcinogenic (Chen and Hao 1998). In addition to human health, toxic metals are harmful for other life forms. Metal ions bioaccumulate in the environment and are magnified along the food chain, leading to more pronounced toxic effects in animals at higher trophic levels. The element Cd accumulates in aquatic organisms *via* dietary or aqueous exposure (Liao *et al*. 2011), with a half-life of 10 to 30 years (Moore and Ramamoorthy 1984). The main mechanism of toxicity is the antagonistic interaction

between the uptake of the Ca^{2+} and Cd^{2+} ions, leading to acute hypocalcemia and growth reduction (McGeer *et al.* 2011).

The toxicity of heavy metals for plants varies by plant species, specific metal, concentration, chemical form, and pH. Some heavy metals (*e.g.*, Cu and Zn) have catalytic properties or act as cofactors or activators in enzyme reactions, while others (*e.g.*, As, Cd, and Hg) have toxic effects on enzymes. Many enzymes contain Zn, which is required to maintain the integrity of ribosomes (Nagajyoti *et al.* 2010). Some heavy metals are essential for animals and plants, such as Fe, Cu, and Zn as micronutrients (Wintz *et al.* 2002), but excess uptake can lead to toxic effects (Monni *et al.* 2000). For example, Cu is an essential micronutrient for living organisms, but it can be toxic at increased levels (Hernández *et al.* 2006). It is essential to plants for photosynthesis, a constituent of the primary electron donor, and a cofactor of several enzymes (Mahmood and Islam 2006). In contrast, the element Fe is a component of hemoglobin, myoglobin, and cytochrome.

Lead (Pb) is a persistent heavy metal characterized as a hazardous priority substance by EU directive 1907/2006 (EC 2006). Concentrations of Pb have increased in the environment due to anthropogenic activities (Mager 2011; Sfakianakis *et al.* 2015). The bioavailability of Pb depends on its adsorption into the sediment, the content of organic matter in water, pH, alkalinity, and hardness (Sepe *et al.* 2003; Mager 2011), with the Pb^{2+} ion being the most toxic form. At high levels, Pb causes encephalopathy, cognitive impairment, anemia, kidney damage, and behavioral disturbances (Pagliuca and Mufti 1990).

BIOSORPTION

Biosorption can be defined as an ability of certain biomass to bind and concentrate heavy metals from even dilute aqueous solutions. In particular, the cell wall structure exhibits this property (Ahluwalia and Goyal 2007). Biosorption involves a solid sorbent, liquid phase, and the dissolved species to be sorbed. Biomass behaves as an ion-exchanger, taking only from minutes to a few hours to achieve an efficient metal uptake (Ahluwalia and Goyal 2007).

Many methods have been developed to remove heavy metals from effluents, but especially in the mining industry, mixtures of heavy metals in aqueous solutions pose challenges for traditional water treatment methods. Conventionally, heavy metals have been removed by precipitation, filtration, ion exchange, reverse osmosis, and electrodialysis ultrafiltration from aqueous solutions, or they have been adsorbed by activated carbon (Patterson 1985; Das *et al.* 2008). For example, by increasing the effluent pH, soluble metals can be converted into insoluble hydroxides. Unfortunately, chemical precipitation is ineffective, especially at low concentrations (< 50 mg L^{-1}), while ion exchange, membrane, and adsorption processes have high operating costs (Das *et al.* 2008). Additionally, many traditional methods produce large amounts of sludge that requires further treatment (Sud *et al.* 2008). Activated carbon is a widely used adsorbent for the removal of heavy metals, but its use suffers from high operating costs and complex thermal regeneration (Hokkanen *et al.* 2013).

Biosorption can be a cost-effective alternative and is appropriate for removing metals from effluents (Sud *et al.* 2008). Biosorbents are readily available and can remove heavy metals at concentrations as low as 1 mg per ton (Montes-Atenas and Schroeder

2015), often unattainable by conventional methods. The main advantages of biosorption over conventional methods are the low cost of renewable organic material, the minimal use of chemicals, the possibility of metal recovery, and the regeneration of the biosorbent (Bailey *et al*. 1999; Vieira and Volesky 2000). In recent decades, a high number of studies have been conducted to find inexpensive and sustainable sorbent materials for the removal of heavy metal species from aqueous solutions (Al-Asheh *et al*. 2003; Cao *et al*. 2004; Jang *et al*. 2005). However, little effort has been made to design economically viable industrial applications (Sud *et al*. 2008). Seaweeds, molds, yeasts, other microbial biomass, and agricultural waste have been widely explored (Zhou and Kiff 1991; Bailey *et al*. 1999; Sudha and Abraham 2003), but recently the focus has been on studying waste and the by-products of large-scale industrial operations. Materials containing cellulose especially show potential in metal binding. Wood-based biomass has a suitable chemical composition, is renewable, abundant, and an economical option for adsorbing heavy metals.

Biosorbents

Different biomass materials have been investigated as potential biosorbents for heavy metals. Such applications have been reviewed by Hubbe *et al.* (2011). Potential biosorbants include sawdust (Bryant *et al*. 1992; Volesky and Holan 1995), pine bark and needles (Vàzque *et al*. 1994), canola meal (Al-Asheh and Duvnjuk 1998; Al-Asheh *et al*. 1998), rice straw, soybean hulls, sugarcane bagasse, and peanut shells (Johns *et al*. 1998). Saeed *et al*. (2005) used papaya wood, generated as waste in papaya plantations with no other commercial use, to bind metals; the wood showed a high efficiency in removing heavy metals from aqueous solutions (Saeed *et al*. 2005). Additionally, biosorption of metals has been reported in a variety of biomaterials, including microalgae, seaweed, bacteria, fungi, and crop residues (Saeed *et al*. 2002). Some logging waste has been studied as a biosorbent, such as plant bark (*Acacia arabica*, eucalyptus) and pine needles, showing 90 to 100% for Cr removal efficiencies (Mohan *et al*. 2006; Sarin and Pant 2006; Venkateswarlu *et al*. 2007).

Lignocellulosic biosorbents produced as waste material and by-products of various industries have been used to adsorb metals ions from aqueous solutions. For example, mechanically treated peach stone particles have been used to bind copper ions from aqueous solutions (Lopičić *et al*. 2017). Peach stone particles showed interactions between copper ions and carboxyl and hydroxyl groups. Similarly, apricot (*Prunus armeniaca*) shells produced as waste product in fruit processing were able to adsorb copper, zinc, and lead ions (Cu^{2+}, Zn^{2+}, and Pb^{2+}) after an alkali treatment (Šoštarićc *et al*. 2018). Vilardi *et al*. (2018) reported use of olive stones, the main solid waste from the olive oil industry, coated by iron and magnetite nanoparticles in binding Cr(VI) from aqueous solutions. Additionally, crushed chili seeds (*Capsicum annuum*) have been used to adsorb cadmium and lead ions (Cd^{2+}, Pb^{2+}) from aqueous solutions (Medellin-Castillo *et al*. 2017). They found that elevated pH and temperature increased electrostatic interactions between the negatively charged surfaces and the metal cations. Khan and Rao (2017) reported that copper and nickel ions can be adsorbed from wastewater by alkali treated butternut (*Cucurbita moschata*) biomass. The treatment increased the acidic functional groups on the surface of the biomass and led to increased adsorption efficiencies of copper and nickel.

Even less common agricultural waste has been tested (Cimino *et al*. 2000; Annadurai *et al*. 2002; Reddad *et al*. 2002b; Hashem *et al*. 2006a, 2006b), such as banana

and orange peels, hazelnut shells, cellulose pulp, cotton stalks, particles of palm trees, and sugar beet pulp. Demirbaş (2008) showed that a biosorbent made of agricultural by-products can be used to remove heavy metals from industrial and municipal wastewater. The use of other plant parts as adsorbents, such as pea peels, fig leaves, broad beans, medlar peels, and jackfruits has shown high removal efficiencies at acidic pH levels (Benaissa 2006). Additionally, marine algal, coffee residues with clay, and cocoa shells have been effective as natural sorbents in binding metal ions from aqueous solutions (Boonamnuayvitaya *et al*. 2004; Meunier *et al*. 2004; Sheng *et al*. 2004).

Cellulose is a renewable, abundantly available biopolymer. However, there are few functional groups in the cellulose fiber that can bind heavy metals. Therefore, a derivatization is required to build binding sites (Navarro *et al*. 2001), for example, by catalytic and selective oxidation of primary hydroxyl groups (Isogai and Kato 1998), or succinylation (Gellerstedt *et al*. 2000). Modified cellulose has scarcely been studied as an adsorbent for heavy metals. However, Hokkanen *et al*. (2013) studied modified micro- and nanocellulose as an adsorbent for binding Zn, Ni, Cu, Co, and Cd in aqueous solutions. They found that the succinic anhydride modification of nanocellulose was effective in binding metals with a regeneration ability of 96 to 100%, showing potential for water treatment applications.

Typically, heavy metals are associated with finer-sized particle classes, the highest metal concentrations are in the less than 1 mm cluster (Sharma *et al*. 1997; Bardos 2004). Therefore, mechanical screening and the removal of the finest fraction have been suggested to produce a final product with an agricultural value (Zennaro *et al*. 2005). Furthermore, Pb is the most strongly bound element in typical organic material (Zheng *et al*. 2004; Reimann 2007), and Ni is the weakest. Lead is taken up by the roots and stored as pyrophosphate in cell walls (Dunn 2007). For example, Dunn *et al*. (1992) reported concentrations of 311 mg kg^{-1} Pb in spruce bark. The spruce bark was collected from Canada, a place distant from any contamination of anthropogenic origin.

Wood bark is mostly used as a combustible material with little added value, but it is also suitable as a sorbent. However, bark naturally contains tannins and other complexation agents that can be released in the solution (Montes-Atenas and Schroeder 2015). Therefore, a pretreatment of bark is required to inactivate the complexation agents. Acid activation increases the adsorption capacity, but the activation in acidic media varies depending on the activating agent, concentration, and temperature (Palma *et al*. 2003). Montes-Atenas and Schroeder (2015) showed that adsorption of Pb on pine bark (*Pinus radiata*) can achieve almost 100% removal of Pb(II) from a 100 mg L^{-1} solution. They concluded that the sorption mainly takes place at the lignocellulosic C-O groups, while adsorption occurs at the phenolic sites. Su (2012) studied the sorption properties of metal ions in tree-related materials. Bark material showed the highest sorption capacity for metal ions, while the lowest was in wood sawdust. Su concluded that the sorption capacity of metals on wood material decreases in the following order: $Fe^{3+} \gg Pb^{2+} \gg Cu^{2+} \gg Fe^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+} > Ba^{2+} \geq Ca^{2+} \geq Mn^{2+} \geq Sr^{2+} > Mg^{2+} > Rb^+ \sim K^+ \sim Na^+ \sim Li+$ and $Fe^{3+} \gg Pb^{2+} > Cu^{2+} \gg Cd^{2+} > Zn^{2+} > Ni^{2+} > Ba^{2+} > Ca^{2+} > Sr^{2+} > Mn^{2+} > Mg^{2+} > K^+ \sim Na^+ \sim Li^+$ for bark material.

Scots pine *Pinus sylvestris* (Taty-Costodes *et al*. 2003) and rubber wood sawdust (Raji *et al*. 1997) have shown 85 to 90% removal efficiencies of heavy metals, at an optimal pH of 5 to 6. Ucun *et al*. (2002) used the cone biomass of *P. sylvestris* as a biosorbent for Cr removal from artificial wastewater. They reported a high adsorption capacity of 84%, with the highest level detected at an acidic pH level of 1.0. Similarly,

Nuhoglu and Oguz (2003) used cone biomass of oriental thuja (*Thuja orientalis*) as a biosorbent for the removal of Cu from aqueous effluents. However, they detected increased sorption at a neutral pH level of 7.7 and 98% adsorption of Cu(II).

Biosorption Process

Biosorption is a complex process, comprising of chemisorption, complexation, adsorption on surface and pores, ion exchange, chelation and adsorption due to physical forces on chemically active sites or functional groups (Volesky 2003), and entrapment by inter- and intrafibrillary capillaries as a result of concentration gradient and diffusion (Sarkanen and Ludwig 1971; Qaiser *et al.* 2007). Metal ions can be sequestered in biomass by, *e.g.*, acetamide, amino, phosphate, amide, amine, sulfhydryl, and carboxyl groups (Ahluwalia and Goyal 2007). The binding capacity of a biomass is often in the same range with synthetic cation-exchange resins (Wase and Foster 1997). However, the early saturation of biomass may be a problem or have the ability to biologically alter the metal valence state.

Typically, the metal uptake by biosorption proceeds in the passive mode (Madrid and Cámara 1997). Passive, not metabolically mediated biosorption is a dynamic reversible adsorption-desorption process, able to bind metal ions by (dead) biomass from solution. Metal ions are adsorbed onto the surface of biomass due to interactions between the metals and the functional groups of biomass (Das *et al.* 2008). In this context, biosorption includes several passive, *i.e.* non-metabolic mechanisms, such as coordination, complexation, ion-exchange, and microprecipitation. It can be distinguished from bioaccumulation, an active, metabolically mediated transport of chemical species.

The type of biomass (living or non-living), the properties of the metal solution, and the ambient conditions affect the mechanism of biosorption. Initial metal concentration, temperature, pH, and biomass concentration are the main factors affecting biosorption. However, at a range of 20 to 35 °C, the temperature seems to be in minor role, with pH being the most important factor (Aksu *et al.* 1992; Pagnanelli *et al.* 2003). An increase in pH leads to decreased competition between protons and metal cations for the same functional groups. Pagnanelli *et al.* (2003) showed that at a pH level of 2, biosorption was minimal, while a sharp increase occurred at pH levels of 3 to 4 (95.5% Cu, 87.7% Cd, and 62.7% Zn). Adsorption can be performed as long as heavy metals remain in the solution, but the maximum adsorption capacity depends on the properties of the ion solution and the adsorbing substrate (Montes *et al.* 2006). Additionally, a decreased positive surface charge leads to a lower repulsion between the surface and metal ions (Reddad *et al.* 2002a).

The usefulness of a biosorbent material depends on its sorption capacity, but also on its regeneration ability and potential to be reused (Bishnoi and Garima 2005), which is important for industrial applications. If sorption occurs on the surface of a biosorbent, desorption occurs more easily *via* simple methods, while an intracellularly bound sorbate requires destructive methods such as incineration or dissolution into strong acids or bases (Gadd and White 1993). Destructive methods are only economical for a cheap biosorbent and recently the aim has been to use non-destructive methods (Vijayaraghavan and Yun 2008).

Modification of biomass

There are several physical and chemical modification methods to enhance the performance of biosorbent materials, including conversion into activated carbon or

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biochar (Ioannidou and Zabaniotou 2007; Suhas *et al*. 2007). Typically, physical modification is simpler and more inexpensive, but often less effective compared to chemical modification. An improved sorption ability can be obtained through modifying functional groups (Vijayaraghavan and Yun 2008; Wan Ngah and Hanafiah 2008). For example, acid washing can enhance the capacity of a biosorbent for cationic metals. Additionally, an increase of functional groups or a formation of new ones can enhance the biosorption capacity (Wan Ngah and Hanafiah 2008). Binding sites can be increased by adding long polymer chains onto the surface of a raw biomass, as was extensively reviewed by O'Connell *et al*. (2008). For living microbial biomass, optimum culture conditions can increase the biosorption capacity (Vijayaraghavan and Yun 2008).

Chemical modification may be required if the unmodified cellulosic biomass has an insufficient content of functional groups to perform well as a biosorbant. Modification is typically based on esterification, etherification, halogenation, or oxidation (O'Connell *et al*. 2008). For example, Low *et al*. (2004) used citric acid anhydride to react with cellulose hydroxyl groups, leading to esterification. The increased carboxylic content of the fiber surface was able to increase the sorption potential for divalent metal ions. Halogenation can be performed by reacting cellulose and bromine, yielding 6-bromo-6-deoxycellulose and finally 6-deoxy-6-mercaptocellulose, with its S-substituted derivatives (Aoki *et al*. 1999). The adsorption properties of cellulose can be improved *via* oxidation, for example, periodate oxidation yielding cellulose-hydroxamic derivatives (Maekawa and Koshijima 1990). Finally, etherification is achieved by reacting alkali cellulose with organic halides, such as epichlorohydrin, and yielding epoxy groups for further reactions with a chelating agent (Navarro *et al*. 1996).

Industrial applications

Biosorption can work in batches or be continuous. The choice depends on the physical characteristics of the biosorbent, hydraulic flow, the type of target pollutant, plant space, and invested capital. Many alternatives have been investigated, such as stirred tank reactors, up-flow or down-flow packed bed reactors, fluidized bed reactors, rotating contactors, trickle filters, and airlift reactors (Atkinson *et al*. 1998; Malik 2004). Theoretically, the down-flow packed bed reactor is the most effective among the continuous process options. This is due to gravitational forces transferring water through the bed (Atkinson *et al*. 1998). Additionally, the column biosorption reactor is suitable for pollutant removal in a continuous mode (Volesky 2007). More recently, biosorption *via* biofunctional magnetic beads has been suggested (Li *et al*. 2008). Beads made of *Rhizopus cohnii* and Fe_3O_4 particles coated with alginate and polyvinyl alcohol were able to host Cr biosorption in the form of Cr(VI). Groups of NH_3^+, NH_2^+, and NH were the main binding sites of the Cr ions.

For industrial applications, the main factors affecting biosorption are solution pH, temperature, ionic strength, initial pollutant concentration, biosorbent dosage, biosorbent size, agitation speed, and the coexistence of other pollutants (Park *et al*. 2010), of which pH is the most important. It affects the solution chemistry, activity of the functional groups in the biosorbent, and the competition with coexisting ions (Vijayaraghavan and Yun 2008). Generally, an increase in pH leads to the enhanced removal of cationic metals and reduced removal in the case of anionic metals. Biosorption is typically enhanced as the temperature increases through increased kinetic energy and surface activity (Vijayaraghavan and Yun 2008), but an excessively high temperature can damage the biosorbent material's surface.

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Alkali metals, especially K and Na, are present naturally in biomass (Turn *et al*. 1997). For plant growth, alkali and alkaline earth metals are important nutrients, and typically present at low (ppt to ppm) levels. Alkali and alkaline earth metals often remain in the harvested plant material and react easily with other inorganics, such as silica, S, and Cl, forming deposits and exhibiting corrosion in facilities utilizing biomass (Wang *et al*. 2015a). Deposits are known to be composed of K, Ca silicate, chlorides, sulfates, carbonates, and hydrates. In combustion systems, alkali compounds foul heat transfer surfaces, leading to slag formation in grate-fired units and the formation of agglomerates in fluidized beds. Additionally, the formation of alkali vapor on turbine surfaces may lead to hot corrosion. The Cl-based corrosion is affected by temperature as well as the concentrations of alkali metal, Cl, S, and oxygen, as reviewed by Nielsen *et al*. (2000). For example, Cl can influence the corrosion by forming Cl_2, HCl, NaCl, and KCl, causing direct corrosion *via* the oxidation of metal alloys. Alkali compounds are largely water soluble and can be removed by mechanical and leaching methods (Kinoshita *et al*. 1991).

The first patents for specific types of biosorbents were applied for in the early 1980s. In the 1990s, commercial biomaterials were developed, such as BIO–FIX, AlgaSORB™ (*C. vulgaris*), and AMT-BIOCLAIM™ (*Bacillus* biomass) (Volesky 1990; Garnham 1997), for the removal of heavy metal ions from industrial or mining wastewater. The BIO–FIX sorbent can bind heavy metal ions from industrial wastewater and incorporate a biomass of cyanobacteria (*Spirulina*), yeasts, algae, or plants (*Lemna* sp., *Sphagnum* sp.), immobilized in polymeric (polysulphone, polyethylene, and polypropylene) porous beads (Tsezos *et al*. 2012). In contrast, Advanced Mineral Technologies Inc. used AMT-BIOCLAIM™ from an industrial fermentation process (*Bacillus subtilis*) and achieved a more than 99% removal efficiency of heavy metals from wastewater (Brierley 1990; Eccles 1995). Finally, MetaGeneR and RAHCO Bio-Beads have also used biosorbents for the removal of heavy metals in commercial-scale plants (Chojnacka 2010).

Companies in North America have developed these biosorption processes. In Colorado, Advance Minera Technologies Inc. developed a biosorbent based on Bacillus sp. for metal removal, but production was suppressed in 1988. In Canada, a company named B. V. Sorbex Inc. produced different types of biomaterials based on algae (*S. natans*, *A. nodosum*, *Halimeda opuntia*, *Palmyra pamata*, *Chondrus crispus*, and *C. vulgaris*).

The first pilot plant installations, and some commercial-scale units, of biosorption technology have been constructed in the USA and Canada (Tsezos 1999, 2001). Among pilot-scale experiments, Zouboulis *et al*. (2002) used biosorptive flotation in 10-L columns to remove heavy metals from an aqueous solution with grape stalks from the wine industry. Artola *et al*. (2001) achieved a removal of Cu through using anaerobically digested sludge in a small pilot plant. For example, the biosorption of uranium and other pollutants has been tested and its applicability for the sequestering of metals and recovery has been confirmed (Volesky and Tsezos 1982).

In full-scale applications, the biosorption of metals is often based on peat-based biosorbents (Wase *et al*. 1997). Wastewater treatment using a peat biosorbent has been utilized in Maine, Alaska, Canada, and Ireland. For example, Harrison Western Environmental Services Inc. in Lakewood, Colorado used an application of peat moss capsules to bind As, Cd, Pb, Ni, and Se from wastewater. However, there were difficulties in regeneration, reusing biomass, and obtaining a constant supply of

inexpensive raw material, while other attempts to commercialize biomass biosorption for wastewater treatment and the recovery of metals have not been successful (Tsezos and Noh 1987; Brierley *et al*. 1990, 1991).

Biosorption has been widely tested on a laboratory and pilot scale. However, the transfer of knowledge from laboratory-scale to large-scale industrial applications is a relatively slow process. Many biosorption processes are still being developed and patented for commercial use, but a very limited number of industrial processes or products in the biosorption area have been implemented. Thus far, there are no industrial full-size plants using commercialized biosorbents or wood-based biomass (Park *et al*. 2010). Some biosorbents have been commercialized as adsorbents for metals from aqueous solutions, mostly of algal or microbial origin, but according to the authors' knowledge, there are no industrial processes utilizing wood-based biomass.

Biochar

Biochar is typically defined as a non-liquefied carbonaceous solid material produced in the thermal decomposition of biomass in an oxygen-limited environment. Several studies have shown the ability of biochar to immobilize organic and inorganic pollutants (Lattao *et al*. 2014; Mohan *et al*. 2014; Inyang *et al*. 2015). Previously, biochar has been used for soil amendment (Chan *et al*. 2008; Abdel-Fattah *et al*. 2015) and as a long-term carbon sequestration agent (Wilson *et al*. 2009), but it also has adsorption potential for heavy metals in aqueous solutions (Chen *et al*. 2011; Mahmoud *et al*. 2012; Regmi *et al*. 2012).

Biochar can be produced from a variety of feedstock materials, such as industrial by-products, and agricultural and forest residues, but even from unconventional materials, such as municipal solid waste (Hwang *et al*. 2008), food waste (Rhee and Park 2010), newspapers (Li and Zhang 2004), and bones (Dimović *et al*. 2011). Additionally, biochar can be produced from animal waste, such as poultry litter and dairy manure (Duku *et al*. 2011). The main advantage of these materials is their low cost and abundance. Most forest residues are generated as by-products and waste from harvesting for bioenergy production, which are often scarcely utilized for other purposes. Recently, biochar made of industrial waste has raised interest due to its wide availability and low cost (Yao *et al*. 2011a, 2011b). During the production of biofuels, biochar is produced as a by-product and numerous studies have been conducted regarding the development of lignocellulosic non-food biomass into biofuels (Balan *et al*. 2013).

Biochar has a porous aromatic surface with oxygen-containing functional groups that play a crucial role in trapping metals (Abdel-Fattah *et al*. 2015). Typically, biochar has a large surface area with a network of micropores (< 2 nm), mesopores (2 to 50 nm), and macropores (> 50 nm) (Mukherjee *et al*. 2011). Biochar can adsorb metals, such as Pb, Cu, Ni, Cd, Hg, and As from aqueous solutions (Budinova *et al*. 2006; Amuda *et al*. 2007; Cao *et al*. 2009; Uchimiya *et al*. 2010, 2011). Heavy metals can be absorbed by raw biomass, for example, peat or sawdust (Hu *et al*. 2008; Sevilla and Fuertes 2009), but it carries the risk of leaching and metal remobilization (Liu and Zhang 2009). In contrast, biochar does not lead to such risks. Adsorption on biochar is strongly affected by the solution pH level, due its effects on the surface hydroxyl groups (Stumm 1992).

Uschmiya *et al*. (2011) studied the retention of Cu, Ni, Cd, and Pb by biochar made of broiler litter manure. Paradelo and Barral (2012) used biochar produced from municipal solid waste to study their retention of Cu, Zn, and Pb. Mohan *et al*. (2007) tested the adsorption of toxic materials with fast pyrolysis biochar from oak and pine bark

as well as from wood. The authors concluded that the maximum adsorption occurred at pH levels of 3 to 4 for As and at levels of 4 to 5 for Pb and Ca; they also found that the adsorption of biochar occurred *via* ion-exchange. Adsorption into the biochar strongly depends on the structure and chemical properties, which are a function of pyrolysis and activation processes (Han *et al*. 2013). Inyang *et al*. (2011) showed that biochar from anaerobically digested sugarcane bagasse is a more effective sorbent for Pb than undigested or activated carbon. Inyang *et al*. (2012) studied the sorption of heavy metals by biochar made of anaerobically digested dairy waste and sugar beet. They concluded that biochar is a suitable sorbent to remove Ni, Cu, Cd, and Pb from wastewater.

Production

There are several ways to produce biochar from biomass, including slow pyrolysis, flash pyrolysis, and hydrothermal conversion. During slow pyrolysis, biomass is heated for an extended period of time (5 to 30 min) at 400 to 500 °C without oxygen, while moderate pyrolysis proceeds at approximately 500 °C for 10 to 20 s and fast pyrolysis occurs for 1 s (Kumar *et al*. 2011). Generally, temperatures over 650 °C favor the formation of gaseous products, while slower heating rates with moderate maximum temperatures lead to maximized char yield (Kumar *et al*. 2011). Biochar produced at a higher temperature has a high pH and surface area (Lehmann 2007), while lower temperatures lead to a higher oxygen content and more active sites for binding (Kumar *et al*. 2011). For example, Abdel-Fattah *et al*. (2015) studied biochar produced from pinewood waste *via* slow pyrolysis. The authors found that the biochar was effective in removing metal contaminants (Mg, Ca, Cr, and Pb ions) from drinking water and leather tannery effluent at up to 91.6% removal efficiencies.

Various methods of biochar production, including the pretreatment of feedstock or the modification of char surface, have led to efficient biochar types with good adsorption capacity that, in some cases, are even better than those of commercial activated carbons (Inyang *et al*. 2011, 2012). It has been reported that the removal efficiency of Pb and Cd with oak bark is similar to that of a commercial activated carbon (Calgon F-400) (Mohan *et al*. 2007). Furthermore, the sorption capacity of biochar can be enhanced by esterification (Tan *et al*. 1993). For example, physical treatment *via* the pulverization of feedstock prior to pyrolysis can enhance the sorption ability in aqueous solutions (Tong *et al*. 2011). Applications of biochar in binding contaminants in soils have been extensively reviewed by Kookana (2010) and Beesley *et al*. (2011), while the production of biochar has been reviewed by Mohan *et al*. (2014) and Ahmad *et al*. (2014).

Chemistry of Sorption

Native wood and other wood-based biomass are mostly composed of lignin and cellulose, hemicellulose, extractives, lipids, proteins, sugars, starches, water, hydrocarbons, and inorganics. In general, the functional groups of a biosorbent attract and sequester heavy metals. Functional groups, such as amide, amine, carbonyl, carboxyl, esters, hydroxyl, imine, imidazole, sulfonate, sulfhydryl, thioether, phenolic, phosphate, and phosphodiester groups enable biosorption (Gupta *et al*. 2000; Vieira and Volesky 2000; Sud *et al*. 2008). Additionally, steric, conformational, and other barrier properties can have an effect on the sorption process (Volesky 1994). Biosorption occurs *via* chemical and physical mechanisms, such as ion exchange, complexation, adsorption, precipitation, and entrapment in inner capillaries (Sud *et al*. 2008).

The carboxyl groups are mainly uronic in acid type, chemically bound to xylan hemicellulose, or are found in pectin. Carboxyl groups can also be found in native lignin and extractives (Bhardwaj *et al*. 2004). Phenolic hydroxyl groups mostly originate from lignin. Uronic acid groups often originate from 4-O-methyl glucuronic acid units in xylan and D-galacturonic acid units in pectins, but also in D-glucuronic acid in arabinogalactan (Laine *et al*. 1996; Koljonen *et al*. 2004). In different wood species, these groups are mostly methyl-esterified and lactonized (Konn *et al*. 2007). The molar ratio of glucuronic acid to xylan is approximately 1:5 in softwood and 10:1 in hardwood (Fengel and Wegener 1989; Lindström 1992). On average, there is 1.5 times more hemicellulose in hardwood than in softwood.

The binding occurs in phenol and carboxyl groups, in which phenolic groups originate from residual lignin. The affinity of metal ions to lignin is much higher than to that of carbohydrates (Perat *et al*. 2001; Carrot and Carrot 2007). Most carboxylic groups in pulp are hexenuronic acids that are formed during kraft cooking (Buchert *et al*. 1995; Devenyns and Chaveheid 1997). Granholm *et al*. (2010) studied the chelation of hardwood and softwood kraft pulp. Many elements in kraft pulp were detected and the highest concentrations of elements (Na, Ca, Mg, Mn, and K) in hardwood pulp ranged between 48 and 750 ppm, while only trace amounts of As, Rb, zirconium (Zr), and Sn (0.04 to 0.11 ppm) were found.

Many studies have shown the importance of carboxylic groups in the sorption of metal ions to biomass material (Bakir *et al*. 2009; Hubbe *et al*. 2011). Wood and bark can have ion-exchange properties due to certain anionic functional groups. These functional groups include mostly phenolic hydroxyl groups and carboxyl groups, acting as binding sites of metal ions to wood and bark. Some remain during pulping and bleaching, while some new groups are formed in these processes (Fardim and Holmbom 2003). Additionally, the number and type of functional groups is higher in mechanical pulp compared to chemical pulp, due to lignin carrying the phenolic hydroxyl groups. However, in chemical pulp the binding sites are more evenly distributed.

Sorption mechanisms of biochar

The sorption ability of biochar is due to the surface properties that originate from feedstock material. Oxygen-containing groups, such as hydroxyl, carboxyl, and ether groups, for example, in oak bark biochar, originate from polyphenolic tannins, flavonoids, and suberin in bark. They give negatively charged surface sites for the biochar that can attract positively charged metal ions (Mohan *et al*. 2007). The pyrolysis of agricultural residues, such as sugar beet tailings, can lead to electron donor functional groups, due to the heteropolysaccharides of the feedstock (Aksu and Isoglu 2005). For example, hydroxyl, carboxyl, and ether functional groups allow the sorption of Cr (Dong *et al*. 2011).

Precipitation, complexation, ion exchange, physical sorption, and chemisorption are among the mechanisms that lead to the removal of heavy metals from aqueous solutions by biochar. Precipitation is the formation of solid compounds in a solution or on a surface during the sorption process. It is one of the main mechanisms binding heavy metals by biochar materials. In complexation, multi-atom structures are formed with specific metal-ligand interactions that are important for metals with partly filled d-orbitals with an affinity for ligands, such as transition metals (Crabtree 2009).

Heavy metals can be bound by electrostatic interactions with a biochar surface. High temperatures in carbonization promote graphene structures in biochar that favor

electrostatic attractions (Keiluweit and Kleber 2009). In contrast, ion exchange on biochar begins *via* the selective replacement of positively charged ions, such as Na, Li, K, Ca, and Be, on biochar. High levels of cationic nutrients in wood material can yield a high cation-exchange capacity of the biochar and enhance the sorption of metal ions, for example, Pb in acidic conditions (Mohan *et al*. 2007). Finally, sorption can occur due to the physical sorption of metal ions into the sorbent pores without the formation of chemical bonds. Inyang *et al*. (2016) have reviewed adsorption kinetics and thermodynamics describing the sorption characteristics of biochar.

ANALYSIS OF METALS

In previous decades, the distribution of free metals and their binding sites in wood has been determined *via* chemical stains and the autoradiography of radioisotopes. However, these methods are unable to quantify the total metal content. Currently, a large number of analytical tools are available for the detection of active sites for the binding of metals. Some of these tools include infrared absorption spectroscopy (IR) or Fourier transform infrared spectroscopy (FTIR) (Memon *et al*. 2008), scanning electron microscopy (SEM) (Memon *et al*. 2008), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) analysis, electron spin resonance spectroscopy (ESR), nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), and chemical fractionation analysis (CFA) (Werkelin *et al*. 2010).

Metal species can be detected using X-ray spectroscopic techniques or a SEM with energy dispersive X-ray analysis (SEM-EDX), but X-ray spectroscopic techniques are not sensitive enough for trace metal imaging and often suffer from quantification problems. Sensitivity and quantification are limited by background scatter and abundant matrix elements (Becker *et al*. 2010; Blaske *et al*. 2014), unlike a sensitive graphite furnace atomic absorption spectrometry (GFAAS), which can directly detect heavy metal ions (Mirzaei *et al*. 2011).

Mass spectrometry is one of the most important techniques for the determination of element concentrations at trace and ultratrace levels, for isotope analysis, and for structural characterization. This is mostly due to its high sensitivity and low detection limits (Becker 2007). For example, in bioanalytics, the determination of essential trace metals, metalloids, and non-metals, such as S, P, and Cl is highly important. Many proteins with heteroelements or metals have been detected and quantified by inductively coupled plasma mass spectrometry (ICP-MS) equipment (Tatar *et al*. 2007). Essential and toxic metals are often inhomogenously distributed in biological material, creating the need for analytical techniques with good spatial resolution and a high signal-to-noise ratio.

Before ICP-MS techniques were established, imaging techniques, such as X-ray spectroscopy (Majumdar *et al*. 2012) and secondary ion mass spectrometry (SIMS) (Guerquin-Kern *et al*. 2005), were used for solid samples. Secondary ion mass spectrometry provides resolution down to 50 nm with a penetration depth of only 0.2 to 10 nm, but it does not enable elemental quantification. Among ICP-MS methods, laser ablation (LA)-ICP-MS is suitable for the quantification of metals from solid samples down to sub-ppm levels (Tokareva *et al*. 2010); but it provides mostly semi-quantitative results. Examples of different methods are listed in Table 1.

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Table 1. Examples of Analysis Methods Applied to Study Metals in Aqueous Matrices and Wood-Based Biomass

Method of Analysis	Sample Matrix	Detection Limits (LOD); Elements	Reference
ETAAS	Flowers, leaves, stem, roots	0.01 μg g^{-1}; Co, Cu, Ni	Takuwa *et al.* (1997)
FTIR-EDX, SEM-EDX	Industrial wastewater	1.7×10^{-3} mg L^{-1}; Cd(II)	Memon *et al.* (2008)
CFA	Biomass of spruce, pine, birch, aspen	nd; e.g. Ca, K, Na, Mg, Mn	Werkelin *et al.* (2010)
LA-ICP-MS	Wood fiber	Semi-quantitative mg kg^{-1}; Cu, Mg, Sr, Zn	Tokareva *et al.* (2010)
HPLC-ICP-MS	Groundwater	5-10 ng L^{-1}; (As III, As V)	Amman *et al.* (2010)
DLLME-GFAAS	Water, wastewater	0.2 ng L^{-1} Cr(III); 1.3 ng L^{-1} Co, Ni, Pb	Mirzaei *et al.* (2011)
SPE-ICP-OES	Vegetables	0.67 Cd(II); 0.82 Co(II) ng mL^{-1} (LOQ)	Özdemir *et al.* (2012)
ICP-OES	Norway spruce stem, bark, twigs	nd; Al, Ca, K, Na, Si, P, Zn	Wang and Dibdiakova (2014)
SEM-EDX, XRD	Norway spruce stem, bark, twigs	nd; CaO, MgO, K$_2$SO$_4$, CaSiO$_3$, Ca$_5$(PO$_4$)$_3$	Wang and Dibdiakova (2014)
Pre-concentration (Chelex-100)-ICP-MS	Seawater	5 to 345 ng L^{-1}; As, Cd, Co, Cu, Mn, Ni, Pb, Zn, V	Søndergaar *et al.* (2015)
SEM-EDX	Forest residues	semi-quantitative; Ca, K, Si	Wang *et al.* (2015b)

Iminodiacetate chelating resin (Chelex-100), Chemical fractionation analysis (CFA), dispersive liquid–liquid microextraction (DLLME), electrothermal atomic absorption spectrometry (ETAAS), energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR), graphite furnace atomic absorption spectrometry (GFAAS), high performance liquid chromatography (HPLC), inductively coupled plasma (ICP), laser ablation (LA), limit of detection (LOD), mass spectrometry (MS), optical emission spectrometry (OES), quantitation (LOQ), scanning electron microscopy (SEM), secondary ion mass spectrometry (SIMS), solid phase extraction (SPE), X-Ray diffractometry (XRD) ; nd - not determined

ICP Analysis

Technology for ICP-based methods was first developed in the 1960s, and the first application of induction plasma was described by Bâdârâu *et al*. (1956). The first commercial spectrometers were sold in the mid-1970s. Plasma is an electrically neutral gas composed of ions, electrons, and neutrals, often produced by argon and energized by a high electromagnetic field or a direct current. In ICP analysis, the sample is acidified and sprayed into the plasma for ionization. A high plasma temperature atomizes and ionizes all forms of compounds and gives a reproducible response. Currently, ICP is the most widely used plasma source and is routinely used in diverse fields of research, including geochemistry, the environment, industry, forensic science, and archaeology (Ammann 2007). Typically, ICP analysis is connected with mass spectrometry (MS) (Tokareva *et al*. 2010), optical emission spectrometry (OES) (Álvarez *et al*. 2007), or atomic emission spectrometry (AES) detectors (Nölte 2000).

ICP-OES

Inductively coupled plasma optical emission spectrometry is an atomic spectroscopic technique used for the determination of elements in liquid samples (Su 2012). It can detect more than 70 elements simultaneously over a wide concentration range. The main components of an ICP-OES system include a nebulizer, an ICP torch, and a spectrometer (Boss and Fredeen 1997). Typically, a sample in the liquid phase is transported to the nebulizer through a thin tube. Argon gas is pumped through the nebulizer, which breaks down the droplets into an aerosol. The droplets are transported to a spray chamber between the nebulizer and the torch. Large droplets are removed, while smaller ones of uniform size are injected into the plasma. Atoms and ions are excited by the high temperature of argon plasma (8000 to 10000 K), emitting characteristic radiations at specific wavelengths. Intensities are measured in the detector and converted into concentrations based on the calibration curves of known standards.

The ICP-OES equipment has been widely used in various applications of metal analysis. For example, Özdemir *et al*. (2012) used ICP-OES to detect and quantify Cd and Co ions in vegetables. The authors used fungi *Pleurotus eryngii* as a solid-phase biosorbent on Aberlite XAD-16 to concentrate trace levels of Cd and Co. They found the best performance at a pH level of 5 for Co and a pH level of 6 for Cd. The levels in vegetables (onion, aubergine, and okra) ranged up to 125.6 ng g^{-1} for Cd and up to 98.8 ng g^{-1} for Co. Wang and Dibdiakova (2014) studied levels of Al, Ca, K, Na, Si, and Zn among other elements in stem wood, bark, branches, and twigs of Norway spruce-with a ICP-OES procedure. They found 127 mg kg^{-1} Al, 8.7 mg kg^{-1} K, and 8.1 mg kg^{-1} Na in stem wood. In contrast, Han *et al*. (2013) studied the adsorption of metals into biochar made of wood material with ICP-OES. They found that the relative adsorption capacity of biochar made of softwood was higher compared to that of hardwood biochar.

Previously, application conditions, including the sample input method, radiofrequency, torch configuration, and gas flow (Vanini *et al*. 2015) were optimized, leading to a high number of experiments and a high requirement of reagents and time. Multivariable optimization methods are mathematical-statistical tools that can be used to optimize conditions for an analytical method (Bas and Boyaci 2007; Kumar *et al*. 2014) with a minimum number of experiments (Ferreira *et al*. 2007; Novaes *et al*. 2016). The main advantages of an ICP-OES are the capability of multi-elemental analysis, a large dynamic linear range, low detection limits, and high productivity (Suleiman *et al*. 2008).

ICP-MS

After the introduction of the first commercial instrument in 1983, the ICP-MS technique has been constantly improving and achieving very low detection limits with high spectral resolution (10000) for multielement isotope detection (Nelms 2005). Additionally, ICP-MS is one of the most efficient and element-specific techniques, due to its wide linear range and isotope capability (Pu *et al*. 2005; Zhang *et al*. 2008). Inductively coupled plasma and other types of ion sources of MS, such as ESI, have been reviewed by Lobiński *et al*. (2006). Furthermore, ICP-MS is an ideal tool for the trace analysis of metals, allowing a broad dynamic range up to mg L^{-1} levels, a fast multi-elemental and isotopic analysis with high sensitivity, and detection limits of below 100 ng L^{-1}.

Inductively coupled plasma mass spectrometry has become the method of choice in elemental speciation, including covalently bound elements, coordinated metals, metalloids, and organometallic metabolites (Hirner and Emons 2004). For example, elemental characterization in wines has been conducted by ICP-MS (Marisa *et al*. 1999; Kment *et al*. 2005; Tatar *et al*. 2007), suitable for the fast determination of trace and ultratrace elements (Gonzálvez *et al*. 2008). An ICP is a versatile atomizer and ionizer in temperatures up to 5500 °C (Houk and Praphairaksit 2001). In plasma, chemical bonds are broken and the data regarding the total content of an element is acquired. The response is accurate and species-unspecific, allowing quantitation based on commercially available multielement standards (Zeisler *et al*. 2006). High ion density of argon provides the highest collision rate, generating much higher analyte ion densities compared to other ion sources (Ray *et al*. 2004).

Helium or mixtures of helium and argon are typically used as a carrier gas (Wang *et al*. 2013). A small amount of helium in plasma can reduce the formation of the polyatomic ions of argon. Higher sensitivities can be obtained in wet plasma with nebulized solutions of water and methanol in the carrier gas stream (Fliegel *et al*. 2011). Another strategy to increase spatial resolution is coupling a laser microdissection apparatus (LMD) to an ICP-MS. Such a system was originally designed to isolate specific tissue-material cells. In LMD-ICP-MS, LMD works as an ablation system and is typically equipped with a Nd:YAG laser (at 355 nm wavelength), which provides a highly focused beam with a spot size of 1 µm. Overall, commercial systems give a resolution down to 2 to 5 µm.

There are at least four configurations for the vacuum system for an ICP-MS instrument: a cell entirely within the ion optics, within the mass analyzer chamber, within an additional vacuum chamber, and a cell communicating between the ion optics and the mass analyzer chambers. For a typical ICP-MS instrument, the source gas flow into the ion optics chamber is approximately 10^{19} atoms per second (Tanner 2002). The number of collisions for an ion is the length of the ion traveling in the chamber divided by the mean free path.

The two-dimensional collision cell was first introduced into triple quadrupole mass spectrometry by Yost and Enke (1978). The collision cell is placed between two mass analyzing quadrupoles (Ammann 2007). Ions of interest, parent ions, are mass-selected in the first quadrupole (Q1). The ions are led at a selected energy into the collision cell (Q2), which is pressurized with collision gas. Ions impact with the collision gas, leading to fragmentation and the formation of daughter ions. They are further transmitted to the second mass analyzer (Q3), where the daughter ions are detected. The fragmentation may include one or several collisions. Other modes are also possible,

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including neutral loss scan and parent ion scan. The triple quadrupole is often referred to as a tandem MS (MS/MS), differentiating the devices with higher order multipoles, such as hexapole and octapole (Ammann 2007). In contrast, an ion trap mass spectrometer confines and isolates the parent ion, excites the ion, and induces collision-activated dissociation (CID), trapping the daughter ions with mass analysis (March and Todd 1995). The first application of tandem MS with ICP ion source was reported by Douglas (1989) and aimed to perform CID on polyatomic ions Ar^{2+}, ClO^+, $ArCl^+$, and CeO^+. The collision energy needs to be sufficient to promote fragmentation and exceed the bond strength.

Pretreatment

A variety of separation and pretreatment techniques can be used before a sample is introduced into ICP equipment, including coprecipitation (Akagi and Haraguchi 1990), solvent extraction (Kokšal *et al*. 2002), solid phase extraction (SPE) (Costa *et al*. 2002), and on-line SPE applications (Zougagh *et al*. 2004). For aqueous samples, the pretreatment of metal content for ICP analysis can include microwave-assisted acid digestion (Kment *et al*. 2005; Álvarez *et al*. 2007), thermal digestion in an open reactor (Sperkova and Suchanek 2005; Iglesias *et al*. 2007), sample dilution (Marisa *et al*. 2003; Catarino *et al*. 2006), or dry ashing (Moreno *et al*. 2007). For example, wet digestion is suitable for the partial or total decomposition of organic matter, can be performed in open or closed vessels, and is heated by convective thermal energy or microwave radiation (Gonzálves *et al*. 2008).

Reimann *et al*. (2008) studied the metal contents of wood ash from Norwegian birch (*Betula pubescens*) and spruce (*Picea abies*). The authors leached the samples with nitric acid for 1 h, digested in hot water, and added a modified aqua regia to prepare the samples in HCl before analysis *via* ICP-MS. The authors studied 39 elements of which Zn and Ba were among the highest concentrations and Fe and Hg among the lowest. The heavy metals Cd, Cr, Cu, and Pb were found at levels of 37 to 965 mg kg^{-1}, with large variations between wood species, although they were collected from the same site.

Sample introduction

A large variety of sample introduction systems have been developed for ICP-MS. The most economical is an often-used liquid solution nebulization for sample introduction. Typically, solid samples need to be digested and dissolved to obtain a homogeneous sample. Alternatively, the direct access of solid analytes in laser ablation is a method of choice, with a spatial resolution on the micrometer scale of approximately 1 µm (Günther and Mermet 2000). This is a preferred technique in many fields, such as geology (Heinrich 2006), and material and forensic sciences (Berends-Montero *et al*. 2006). Electrothermal vaporization (ETV) allows for sample preparation *in situ* and sample preconcentration (Grégoire 2000). Compared to liquid samples, LA and ETV have enhanced reproducibility, but only with decreased detection limits (Grinberg *et al*. 2006).

Compared to other techniques, ICP-MS is a relatively inexpensive analytical tool, excluding the higher running costs due to argon consumption. To cover the whole mass range of elements, a quadrupole mass analyzer is required to detect all the isotopes of an element. It gives element-specific results, because an element has one or several isotopes that differ from the others. Detection limits are typically in the ng per liter range without preconcentration and, with a high resolution ICP-MS instrument, even below (Moldovan

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et al. 2004). Approximately 80% of elements are composed of several isotopes, and naturally occurring isotopes are routinely measured. Kinetically fractioned isotope ratios require high-precision ICP-MS with a multicollector detection unit (Wieser and Schwieters 2005). High concentrations can be measured by their low-abundance isotopes to protect the detector.

Isotope analysis

In ICP-MS, multi-element capacity and feasibility of isotopic ratio determinations are important features, which make it an ideal tool for isotope analysis. Isotope dilution mass spectrometry (IDMS) is one of the most accurate methods in trace element and elemental species analysis (Heumann 1992). In IDMS, a known quantity of spike, one of the element isotopes, is added to the sample. The resulting isotope ratio is determined with the mass spectrometer, and only isotope ratios instead of absolute intensities are used to calculate concentrations.

With high accuracy and precision, ICP-IDMS has been applied for different elements (Viczián *et al*. 1990; Buckley and Ihnat 1993). Better result accuracy was achieved with an isotope dilution technique compared to conventional calibration methods. Viczián *et al*. (1990) reported on-line isotope dilution with simultaneous injection of the spike and sample into ICP-MS. Furthermore, IDMS can be performed either with species-specific or species-unspecific spike. For species-specific spike, the structure and composition of the species are known, and analytes are labeled with enriched isotopes. In contrast, for species-unspecific spike, spike is added after the sample and may be in another chemical form, is required of the structure, and composition of different analytes are not exactly known. Other calibration methods, such as standard addition, cannot be applied due to different behavior compared to the sample.

There are numerous reports on As analysis in water by ICP-MS (Chatterjee *et al*. 2000; Roig-Navarro *et al*. 2001; Nakazato *et al*. 2002). However, high levels of chloride can interfere with the analysis, due to the formation of argon chloride ($^{40}Ar^{35}Cl$) in the plasma with the same mass as ^{75}As (Wei *et al*. 2001). To avoid this, sample introduction should be carried out *via* ETV, to increase sensitivity and decrease absolute detection limits (Hung *et al.* 2004).

Seawater samples

The technique of ICP-MS is sensitive to matrix interferences induced by high salt (> 1 g L^{-1}) content, which can cause spectral interference (Marin *et al*. 1997; Sutton *et al*. 1997) and matrix effects due to analytical signal variations. Typically, these include suppression caused by reduced ionization efficiency and the clogging of tubes and cones (Jakubowski and Stuever 1997), but signal enhancement has also been reported (Heitmar *et al*. 1990). Trace elements are difficult to analyze from seawater due to their low concentrations and the influence of matrix elements, such as Na, Mg, Ca, K, and Cl. Specifically, ICP-MS allows for the direct detection of trace elements at the µg L^{-1} level, but interferences caused by seawater limit their detection. Spectral interferences are caused by polyatomic species that cause disturbances in the analyte masses, such as $^{35}C^{16}O^+$ with $^{51}V^+$ or $^{40}Ar^{23}Na^+$ with $^{63}Cu^+$. Additionally, easily ionized matrix elements on the plasma (Na, K) cause signal suppression and signal drift, due to the accumulation of salts on the cones and lenses of ICP-MS. Therefore, a pretreatment is required to concentrate the analyte to improve the detection limit, reduce matrix content, and enhance the analytical conditions (Nicolaï 1999).

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Sample pretreatment by coprecipitation, solvent extraction (Ferreira *et al*. 1997; Wu and Boyle 1997), calibration by internal standard, isotope dilution (Alimonti *et al*. 1997), and alternative sample introduction (electrothermal vaporization, flow injection, or ultrasonic nebulization) are common ways to handle what ICP-MS lacks (Jakubowski and Stuever 1997). Additionally, the subtraction of interfering signal and the limitation of polyatomic species formation are ways to correct spectral interferences (Wu and Boyle 1997). Dilution with pure water can reduce matrix effects, but this often leads to inadequate instrument sensitivity. Therefore, trace elements in seawater samples are often preconcentrated on a chelating resin by rinsing the matrix elements from the resin, eluting the trace elements, and detecting with ICP-MS (Beck *et al*. 2002; Veguería *et al*. 2013). Preconcentration can be performed off-line (Veguería *et al*. 2013; Minami *et al*. 2015) or on-line as part of the ICP-MS work-flow (Sumida *et al*. 2006; Veguería *et al*. 2013). On-line is preferred over the off-line step because it reduces the contamination risks of the latter.

Metal preconcentration and separation from seawater has been investigated with chelation by iminodiacetate chelating resin Chelex-100 (Sarzanini and Mentasti 1997). In 1968, Riley and Taylor (1968) reported the use of Chelex-100, which has been the most-studied resin thus far (Miyazaki and Reimer 1993; Fernández *et al*. 1997). Another resin, CC-1, is a highly cross-linked macroporous copolymer that can withstand pressures above 100 bar and is suitable for high performance liquid chromatography (HPLC) applications (Bettinelli and Spezia 1995; Lu *et al*. 1998). Chelex-100 has a high affinity for most trace elements, and microcolumns filled with Chelex-100 have been applied for the on-line preconcentration of seawater (Rahmi *et al*. 2007). The adsorption is dependent upon pH level, with the optimum at around 6.5 (Pesavento and Biesuz 1997). This is often achieved with a buffer, such as ammonia acetate, before introducing through the column filled with Chelex-100 (Ferrarello *et al*. 2001).

Søndergaard *et al*. (2015) studied trace elements in seawater *via* ICP-MS with on-line preconcentration and a Babington nebulizer, which is suitable for samples with high amounts of salt. They found V, Mn, Co, Ni, Cu, Zn, Cd, and Pb with detection limits of 5 to 345 ng L^{-1}, depending on the element. Excess seawater was pumped through the nebulizer of the ICP-MS during the preconcentration step, and the gas flow was adjusted to pump out the seawater without entering the instrument (Søndergaard *et al*. 2015). Therefore, no changes were required for the sample introduction and only a resin-filled (Chelex-100) microcolumn was added to the sample tube.

SPE-ICP-MS

For metal separation, SPE (Birlik *et al*. 2007; Tuzen and Soylak 2007), HPLC (Grotti *et al*. 2014), and ion chromatography (IC) (Jackson and Bertsch 2001) are the most-used methods. The method of SPE is suitable for a variety of environmental samples with high enrichment factors, including automation of the extraction procedure (Poole 2003). Adsorption materials have a crucial role in SPE. For example, silica gel immobilized with various organic compounds has a metal chelating ability with fast and quantitative sorption and elution (Chang *et al*. 2007), but unfortunately it does not enable specific metal ion selectivity (Jiang *et al*. 2006).

A method called molecular imprinting is used for preparing polymers with high molecular recognition by the polymerization of functional monomers in the presence of the template, the target compound used to prepare the polymer, and excess of the crosslinker. Molecular imprinted polymers (MIB) can rebind and react selectively with

specific target analytes (Haupt 2001). Ion-imprinted polymers (IIPs) and MIBs have many similarities, but IIPs have the affinity for metal ions (Rao *et al*. 2004) and have been developed for SPE applications (Daniel *et al*. 2005). A type of molecular imprinting is a technique called surface molecular imprinting, which yields imprinted polymeric material with multiple accessible sites, high selectivity, and fast mass transfer and binding kinetics (Na *et al*. 2006). Additionally, IIPs prepared by surface printing are suitable for binding, for example, Pd, Ni, Fe, Cd, Zn, and Cu (Zhang *et al*. 2007). Zhang *et al*. (2008) studied a Cr(III)-imprinted modified silica gel sorbent, with 3-(2-aminoethylamino) propyl trimethoxysilane (AAPTS). The surface imprinted material was used as a selective SPE sorbent material to bind Cr(III) in environmental water samples analyzed with ICP-MS. The sorbent was suitable in selectively binding Cr(III) from water with good tolerance to other ions. Additionally, it had fast adsorption and desorption kinetics, and good stability under acidic conditions.

HPLC-ICP-MS

Accurate analytical results are a requirement for the study of the toxicity, bioavailability, and environmental behavior of different species. Various chromatographic methods combined with ICP-MS have become powerful techniques for elemental speciation. The method of HPLC coupled with ICP-MS is a sensitive system for the separation and detection of elemental species. Analysis can be performed without sample enrichment, which may influence the composition of the species in the sample.

For example, Rottmann and Heumann (1994) used HPLC with ICP-MS to study Cu and Mo in natural water. They used the on-line isotope dilution method for elemental characterization and detected pg mL^{-1} levels without a sample preparation step. Species (As III, As IV) have been detected in fish and crustaceans by HPLC coupled with ICP-MS equipment (Rattanachongkiat *et al*. 2004). They detected levels up to 17 µg g^{-1} from a Sn mining area. The HPLC separation was performed as an anion exchange HPLC with a phosphate-based eluent at a pH level of 6 to 7.5. Carignan *et al*. (2001) used HPLC prior to ICP-MS to remove isobaric interference and to eliminate signal suppression in the plasma. The authors analyzed rock samples, including basalt, serpentine, and granite, to detect the rare earth elements uranium (U) and thorium (Th). The authors used LC-ICP-MS and found on average 50.6 ng g^{-1} (Th) and 15.3 ng g^{-1} (U).

Zheng *et al*. (2003) applied anion exchange HPLC coupled with ICP-MS to detect As in the surface water of the Moira River, Canada, and found levels up to 75 ng L^{-1}. The river has been contaminated by heavy metals from a mine since the 1860s. Dos Santos *et al*. (2009) detected organic and inorganic Hg in water and sediment samples. The authors used SPE-HPLC for extraction and separation, coupled with ICP-MS, and found on average 30.7 (Hg^{2+}) and 10.8 ($MeHg^+$) ng L^{-1}. Recently, analysis techniques for elements by small-bore HPLC coupled with ICP-MS were extensively reviewed by Grotti *et al*. (2014).

Therefore, ICP-MS coupled with high-performance separation is expanding in the identification of metal species. Moreover, HPLC offers many variations, such as ion-exchange chromatography, ion-pairing chromatography, and size-exclusion chromatography (SEC), that can be coupled with ICP-MS. Thus far, HPLC can be considered one of the most effective instrumental techniques for speciation analysis (Michalke 2002a,b).

CONCLUDING REMARKS

Biosorbents show great potential for binding heavy metals. The availability of forest residue material and its low price increase its value as a biosorbent. Pilot-scaled and full-size plants have been established that use biosorbents for binding heavy metals, but large-scale plants have not been economically viable. Thus far, wood-based material is not in commercial use, but sorbents based on living biomass, such as algae and bacteria, have been studied and patented. Overall, the main challenge in the near future will be to develop the sorption process at a commercial scale to meet economic demands and solve the process-related issues, including metal recovery and the uninterrupted availability of the sorbent material.

There is an ever-increasing demand for utilizing waste as a raw material in different applications. This often includes the removal of heavy metals and collecting them for other purposes. Costly conventional methods for heavy metal removal from industrial effluents and ever-increasing legislative demands require new methods to be found for their removal. Furthermore, the demand for the monitoring of heavy metal levels set by the EU has increased the demand for effective and reliable analytical methods. This requires both methods and equipment to handle even the most difficult sample matrices. The ICP-MS-based methods have shown an ability to achieve low detection limits and reliability. Such methods can be coupled with other pretreatment methods or separate components, using chromatographic methods to meet the increasing demand for the detection of even the lowest concentrations in the future.

REFERENCES CITED

Abdel-Fattah, T. M., Mahmoud, M. E., Ahmed, S. B., Huff, M. D., Lee, J. W., and Kumar, S. (2015). "Biochar from woody biomass for removing metal contaminants and carbon sequestration," *J. Ind. Eng. Chem*. 22, 103-109. DOI: 10.1016/j.jiec.2014.06.030

Ahluwalia, S. S., and Goyal, D. (2007). "Microbial and plant derived biomass for removal of heavy metals from wastewater," *Bioresource Technol*. 98(12), 2243-2257. DOI: 10.1016/j.biortech.2005.12.006

Ahmad, M., Rajapaksha, A. U., Lim, J., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S., and Ok, Y. (2014). "Biochar as a sorbent for contaminant management in soil and water: A review," *Chemosphere* 99, 19-33. DOI: 10.1016/j.chemosphere.2013.10.071

Akagi, T., and Haraguchi, H. (1990). "Simultaneous multielement determination of trace metals using 10 mL of seawater by inductively coupled plasma atomic emission spectrometry with gallium coprecipitation and microsampling technique," *Anal. Chem*. 62(1), 81-85. DOI: 10.1021/ac00200a015

Aksu, Z., and Isoglu, I. A. (2005). "Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp," *Process. Biochem*. 40(9), 3031-3044. DOI: 10.1016/j.procbio.2005.02.004

Aksu, Z., Sag, Y., and Kutsa, T. (1992). "The biosorpnon of copperod by *C. vulgaris* and *Z. ramigera*," *Environ. Technol*. 13(6), 579-586. DOI: 10.1080/09593339209385186

Al-Asheh, S., Banat, F., and Al-Rousan, D. (2003). "Beneficial reuse of chicken feathers in removal of heavy metals from wastewater," *J. Clean. Prod*. 11(3), 321-326. DOI: 10.1016/S0959-6526(02)00045-8

Al-Asheh, S., and Duvnjuk, Z. (1998). "Binary metal sorption by pine bark: Study of equilibria and mechanisms," *Sep. Sci. Technol*. 33(9), 1303-1329. DOI: 10.1080/01496399808544985

Al-Asheh, S., Lamarche, G., and Duvnjuk, Z. (1998). "Investigation of copper sorption using plant materials," *Water Qual. Res. J. Can*. 33(1), 167-183. DOI: 10.2166/wqrj.1998.010

Alimonti, A., Petrucci, F., Fioravanti, S., Laurenti, F., and Caroli, S. (1997). "Assessment of the content of selected trace elements in serum of term and pre-term newborns by inductively coupled plasma mass spectrometry," *Anal. Chim. Acta* 342(1), 75-81. DOI: 10.1016/S0003-2670(96)00545-4

Álvarez, M., Moreno, I. M., Pichardo, S., Camean, A. M., and Gonzalez, A. G. (2007). "Metallic profiles of Sherry wines using inductively coupled plasma atomic emission spectrometry methods (ICP-AES)," *Sci. Aliment*. 27(1), 83-92. DOI: 10.3166/sda.27.83-92

Ammann, A. A. (2007). "Inductively coupled plasma mass spectrometry (ICP MS): A versatile tool," *J. Mass Spectrom*. 42(4), 419-427. DOI: 10.1002/jms.1206

Amuda, O. S., Giwa, A. A., and Bello, I. A. (2007). "Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon," *Biochem. Eng. J*. 36(2), 174-181. DOI: 10.1016/j.bej.2007.02.013

Annadurai, G., Juang, R. S., and Lee, D. L. (2002). "Adsorption of heavy metals from water using banana and orange peels," *Water Sci. Technol*. 47(1), 185-190. DOI: 10.2166/wst.2003.0049

Aoki, N., Fukushima, K., Kurakata, H., Sakamoto, M., and Furuhata, K. (1999). "6-Deoxy-6-mercaptocellulose and its S-substituted derivatives as sorbents for metal ions," *React. Funct. Polym*. 42(3), 223-233. DOI: 10.1016/S1381-5148(98)00076-5

Artola, A., Martin, M. J., Balaguer, M., and Rigola, M. (2001). "Pilot plant biosorption in an integrated contact–settling system: Application to Cu(II) removal by anaerobically digested sludge," *J. Chem. Technol. Biot*. 76(11), 1141-1146. DOI: 10.1002/jctb.496

Atkinson, B. W., Bux, F., and Kasan, H. C. (1998). "Considerations for application of biosorption technology to remediate metal-contaminated industrial effluents," *Water SA* 24(2), 129-135.

Bâdârâu, E., Giurgea, M., Giurgea, G. H., and Truţa, A. T. H. (1956). "Hochfrequente Fackelentladung als Spektralquelle [High-frequency torch discharge as a spectral source]," *Spectrochim. Acta* 11, 441-447. DOI: 10.1016/S0371-1951(56)80074-X

Bailey, S. E., Olin, T. J., Bricka, R. M., and Adrian, D. D. (1999). "A review of potentially low-cost sorbents for heavy metals," *Water Res*. 33(11), 2469-2479. DOI: 10.1016/S0043-1354(98)00475-8

Bakir, A., McLoughlin, P., Tofail, S. A. M., and Fitzgerald, E. (2009). "Competitive sorption of antimony with zinc, nickel, and aluminum in a seaweed based fixed-bed sorption column," *CLEAN – Soil Air Water* 37(9), 712-719. DOI: 10.1002/clen.200900164

Balan, V., Chiaramonti, D., and Kumar, S. (2013). "Review of US and EU initiatives toward development, demonstration, and commercialization of lignocellulosic biofuels," *Biofuel. Bioprod. Bior*. 7(6), 732-759. DOI: 10.1002/bbb.1436

***bioresources*.com**

Bardos, P. (2004). *Composting of Mechanically Segregated Fractions of Municipal Solid Waste – A Review*, Sita Environmental Trust, Falfield, Bristol, UK.

Bas, D., and Boyaci, I. H. (2007). "Modeling and optimization I: Usability of response surface methodology," *J. Food Eng*. 78(3), 836-845. DOI: 10.1016/j.jfoodeng.2005.11.024

Becker, J. S. (2007). *Inorganic Mass Spectrometry: Principles and Applications*, John Wiley & Sons, Chichester, England.

Becker, J. S., Breuer, U., Hsieh, H. F., Osterholt, T., Kumtabtim, U., Wu, B., Matusch, A., Caruso, J. A., and Qin, Z. Y. (2010). "Bioimaging of metals and biomolecules in mouse heart by laser ablation inductively coupled plasma mass spectrometry and secondary ion mass spectrometry," *Anal. Chem*. 82(22), 9528-9533. DOI: 10.1021/ac102256q

Beesley, L., Moreno-Jimenez, E., Gomez-Eyles, J. L., Harris, E., Robinson, B., and Sizmur, T. (2011). "A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils," *Environ. Pollut*. 159(12), 3269-3282. DOI: 10.1016/j.envpol.2011.07.023

Benaissa, H. (2006). "Screening of new sorbent materials for cadmium removal from aqueous solutions," *J. Hazard. Mater*. 132(2-3), 189-195. DOI: 10.1016/j.jhazmat.2005.07.085

Bengtsson, B. E., Coombs, T. L., and Waldichuk, M. (1979). "Biological variables, especially skeletal deformities in fish, for monitoring marine pollution," *Philos. T. Roy. Soc. B* 286(1015), 457-464. DOI: 10.1098/rstb.1979.0040

Berends-Montero, S., Wiarda, W., De Joode, P., and Van der Peijl, G. (2006). "Forensic analysis of float glass using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS): Validation of a method," *J. Anal. Atom. Spectrom*. 21(11), 1185-1193. DOI: 10.1039/B606109E

Bettinelli, M., and Spezia, S. (1995). "Determination of trace elements in sea water by ion chromatography-inductively coupled plasma mass spectrometry," *J. Chromatogr. A* 709(2), 275-281. DOI: 10.1016/0021-9673(95)00454-U

Bhardwaj, N. K., Duong, T. D., Hoang, V., and Nguyen, K. L. (2004). "Determination of fiber charge components of Lo-solids unbleached kraft pulps," *J. Colloid Interf. Sci*. 274(2), 543-549. DOI: 10.1016/j.jcis.2003.12.062

Birlik, E., Ersöz, A., Açikkalp, E., Denizli, A., and Say, R. (2007). "Cr(III)-imprinted polymeric beads: Sorption and preconcentration studies," *J. Hazard. Mater*. 140(1-2), 110-116. DOI: 10.1016/j.jhazmat.2006.06.141

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

Blaske, F., Reifschneider, O., Gosheger, G., Wehe, C. A., Sperling, M., Karst, U., Hauschild, G., and Höll, G. (2014). "Elemental bioimaging of nanosilver-coated prostheses using X-ray fluorescence spectroscopy and laser ablation-inductively coupled plasma-mass spectrometry," *Anal. Chem*. 86(1), 615-620. DOI: 10.1021/ac4028577

Boonamnuayvitaya, V., Chaiya, C., Tanthapanichakoon, W., and Jarudilokkul, S. (2004). "Removal of heavy metals by adsorbent prepared from pyrolyzed coffee residues and clay," *Sep. Purif. Technol*. 35(1), 11-22. DOI: 10.1016/S1383-5866(03)00110-2

Boss, C. B., and Fredeen, K. J. (1997). *Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry*, Perkin-Elmer, San Jose, CA, USA.

Brierley, J. A. (1990). "Production and application of a Bacillus-based product for use in metals biosorption," in: *Biosorption of Heavy Metals*, B. Volesky (ed.), CRC Press, Boca Raton, FL, pp. 305-312.

Brierley, J. A., Brierley, C. L., Decker, R. F., and Goyak, G. M. (1990). "Metal recovery," U.S. Patent No. 4898827.

Brierley, J. A., Brierley, C. L., Decker, R. F., and Goyak, G. M. (1991). "Metal recovery," U.S. Patent No. 4992179.

Bryant, P. S., Petersen, J. N., Lee, J. M., and Brouns, T. M. (1992). "Sorption of heavy metals by untreated red fir sawdust," *Appl. Biochem. Biotech*. 34(1), 777-788. DOI: 10.1007/BF02920596

Bryers, R. W. (1996). "Fireside slagging, fouling, and high-temperature corrosion of heat transfer surface due to impurities in steam-raising fuels," *Prog. Energ. Combust.* 22(1), 29-120. DOI: 10.1016/0360-1285(95)00012-7

Buchert, J., Teleman, A., Harjunpää, V., Tenkanen, M., Viikari, L., and Vuorinen, T. (1995). "Effect of cooking and bleaching on the structure of xylan in conventional pine kraft pulp," *Tappi J.* 78(11), 125-130.

Buckley, W. T., and Ihnat, M. (1993). "Determination of copper, molybdenum and selenium in biological reference materials by inductively coupled plasma mass spectrometry," *Fresen. J. Anal. Chem.* 345(2-4), 217-220. DOI: 10.1007/BF00322593

Budinova, T., Ekinci, E., Yardim, F., Grimm, A., Bjornbom, E., Minkova, V., and Goranova, M. (2006). "Characterization and application of activated carbon produced by H_3PO_4 and water vapor activation," *Fuel Process Technol.* 87(10), 899-905. DOI: 10.1016/j.fuproc.2006.06.005

Cao, X. D., Ma, L. Q., Gao, B., and Harris, W. (2009). "Dairy-manure derived biochar effectively sorbs lead and atrazine," *Environ. Sci. Technol.* 43(9), 3285-3291. DOI: 10.1021/es803092k

Cao, X. D., Ma, L. Q., Rhue, D. R., and Appel, C. S. (2004). "Mechanisms of lead, copper, and zinc retention by phosphate rock," *Environ. Pollut.* 131(3), 435-444. DOI: 10.1016/j.envpol.2004.03.003

Carignan, J., Hild, P., Mevelle, G., Morel, J., and Yeghicheyan, D. (2001), "Routine analyses of trace elements in geological samples using flow injection and low pressure on-line liquid chromatography coupled to ICP-MS: A study of geochemical reference materials BR, DR-N, UB-N, AN-G and GH," *Geostand. Geoanal. Res.* 25(2-3), 187-198. DOI: 10.1111/j.1751-908X.2001.tb00595.x

Carrot, P. J. M., and Carrot, M. M. L. (2007). "Lignin-from natural adsorbent to activated carbon: A review," *Bioresource Technol.* 98(15), 2301-2312. DOI: 10.1016/j.biortech.2006.08.008

Catarino, S., Curvelo-Garcia, A. S., and Bruno de Sousa, R. (2006). "Measurements of contaminant elements of wines by inductively coupled plasma-mass spectrometry: A comparison of two calibration approach," *Talanta* 70(5), 1073-1080. DOI: 10.1016/j.talanta.2006.02.022

Celik, A., and Demirbaş, A. (2005). "Removal of heavy metal ions from aqueous solutions *via* adsorption onto modified lignin from pulping wastes," *Energ. Source.* 27(12), 1167-1177. DOI: 10.1080/00908310490479583

Chan, K. Y., Van Zwieten, L., Meszaros, I., Downie, A., and Joseph, S. (2008). "Using poultry litter biochars as soil amendments," *Aust. J. Soil Res.* 46(5), 437-444. DOI: 10.1071/SR08036

Chang, X. J., Jiang, N., Zheng, H., He, Q., Hu, Z., Zhai, Y. H., and Cui, Y. M. (2007). "Solid-phase extraction of iron(III) with an ion-imprinted functionalized silica gel sorbent prepared by a surface imprinting technique," *Talanta* 71(1), 38-43. DOI: 10.1016/j.talanta.2006.03.012

Chen, J. M., and Hao, O. J. (1998). "Microbial chromium(VI) reduction," *Crit. Rev. Env. Sci. Tec*. 28(3), 219-251. DOI: 10.1080/10643389891254214

Chen, X. C., Chen, G. C., Chen, L. G., Chen, Y. X., Lehmann, J., McBride, M. B., and Hay, A. G. (2011). "Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution," *Bioresource Technol*. 102(19), 8877-8884. DOI: 10.1016/j.biortech.2011.06.078

Chatterjee, A., Shibata, Y., Yoshinaga, J., and Morita, M. (2000). "Determination of arsenic compounds by high-performance liquid chromatography-ultrasonic nebulizer-high power nitrogen-microwave-induced plasma mass spectrometry: An accepted coupling," *Anal. Chem*. 72(18), 4402-4412. DOI: 10.1021/ac0017077

Chojnacka, K. (2010). "Biosorption and bioaccumulation--The prospects for practical applications," *Environ. Int*. 36(3), 299-307. DOI: 10.1016/j.envint.2009.12.001

Cimino, G., Passerini, A., and Toscano, G. (2000). "Removal of toxic cations and Cr (VI) from aqueous solution by hazelnut shell," *Water Res*. 34(11), 2955-2962. DOI: 10.1016/S0043-1354(00)00048-8

Costa, A. C. S., Lopes, L., Korn, M. G. A., and Portela, J. G. (2002). "Separation and pre-concentration of cadmium, copper, lead, nickel and zinc by solid-liquid extraction of their cocrystallized naphthalene dithizone chelate in saline matrices," *J. Brazil Chem. Soc*. 13(5), 674-678. DOI: 10.1590/S0103-50532002000500022

Crabtree, R. H. (2009). *The Organometallic Chemistry of the Transition Metals*, Wiley, New York, USA.

Crini, G. (2006). "Non-conventional low-cost adsorbents for dye removal: A review," *Bioresource Technol*. 97(9), 1061-1085. DOI: 10.1016/j.biortech.2005.05.001

Daniel, S., Babu, P. E. J., and Rao, T. P. (2005). "Preconcentrative separation of palladium(II) using palladium(II) ion-imprinted polymer particles formed with different quinoline derivatives and evaluation of binding parameters based on adsorption isotherm models," *Talanta* 65(2), 441-452. DOI: 10.1016/j.talanta.2004.06.024

Das, N., Vimala, R., and Karthika, P. (2008). "Biosorption of heavy metals - An overview," *Indian J. Biotechnol*. 7(2), 159-169.

Demirbaş, A. (2008). "Heavy metal adsorption onto agro-based waste materials: A review," *J. Hazard. Mater*. 157(2-3), 220-229. DOI: 10.1016/j.jhazmat.2008.01.024

Devenyns, J., and Chauveheid, E. (1997). "Uronic acids and metals control," in: *Proceedings of 9th International Symposium* on *Wood and Pulping Chemistry*, Montreal, Canada, pp. M5-1-M5-4.

DeWalle, D., Sharpeand, W., and Swistock, B. (1995). *Tree Rings as Indicators of Ecosystem Health*, CRC Press, Boca Raton, FL.

Dimović, S. D., Smičiklas, I. D., Šljivić-Ivanović, M. Z., Plećaš, I. B., and Slavković-Beškoski, L. (2011). "The effect of process parameters on kinetics and mechanisms of Co^{2+} removal by bone char," *J. Environ. Sci. Heal. A* 46(13), 1558-1569. DOI: 10.1080/10934529.2011.609454

Dong, X. L., Ma, L. N. Q., and Li, Y. C. (2011). "Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing," *J. Hazard. Mater*. 190(1-3), 909-915. DOI: 10.1016/j.jhazmat.2011.04.008

Dos Santos, J. S., De la Guárdia, M., Pastor, A., and Dos Santos, M. L. P. (2009). "Determination of organic and inorganic mercury species in water and sediment samples by HPLC on-line coupled with ICP-MS," *Talanta* 80(1), 207-211. DOI: 10.1016/j.talanta.2009.06.053

Douglas, D. J. (1989). "Some current perspectives on ICP-MS," *Can. J. Spectrosc.* 34(2), 38-49. DOI: 10.1007/s00216-009-2658-3

Duku, M. H., Gu, S., and Hagan, E. B. (2011). "Biochar production potential in Ghana - A review," *Renew. Sust. Energ. Rev*. 15(8), 3539-3551. DOI: 10.1016/j.rser.2011.05.010

Dunn, C. E. (2007). *Biogeochemistry in Mineral Exploration*, Volume 9, Elsevier, Amsterdam, Netherlands.

Dunn, C. E., Adcock, S. W., and Spirito, W. A. (1992). *Reconnaissance Biogeochemical Survey Southeastern Cape Breton Island Nova Scotia, Part 1—Black Spruce Bark* (File 2558), Geological Survey Canada, Nova Scotia, Canada.

European Commission (EC) Directive 91/271/EEC (1991). "Council directive 91/271/EEC of 21 May 1991 concerning urban waste water treatment," European Commission, Brussels, Belgium.

EC Directive 2009/28/EC (2009). "Council directive 2009/28/EC of 23 April 2009, on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC," European Commission, Brussels, Belgium.

EC Regulation 1907/2006 (2006). "Commission regulation of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)," European Commission, Brussels, Belgium.

Eccles, H. (1995). "Removal of heavy metals from effluent streams - Why select a biological process?," *Int. Biodeter. Biodegr*. 35(1-3), 5-16. DOI: 10.1016/0964-8305(95)00044-6

Ellis, E. L. (1965). *Cellular Ultrastructure of Woody Plants*, Syracuse University Press, Syracuse, New York, USA.

Faaij, A. P. C. (2004). "Biomass combustion," in: *Encyclopedia of Energy*, C. J. Cleveland (ed.), Elsevier, New York, USA, pp. 175-191.

Fardim, P., and Holmbom, B. (2003). "Fast determination of anionic groups in different pulp fiber by methylene blue sorption," *Tappi J*. 2(10), 28-32.

Fengel, D., and Wegener, G. (1989). *Wood - Chemistry, Ultrastructure, Reactions*, De Gruyter, New York, USA.

Fernández, F. M., Stripeikis, J. D., Tudino, M. B., and Troccoli, O. E. (1997). "Fully automatic on-line separation preconcentration system for electrothermal atomic absorption spectrometry: Determination of cadmium and lead in sea-water," *Analyst* 122(7), 679-684. DOI: 10.1039/A607598C

Ferrarello, C. N., Bayon, M. M., Alonso, J. I. C., and Sanz-Medel, A. (2001). "Comparison of metal pre-concentration on immobilized Kelex-100 and quadruple inductively coupled plasma mass spectrometric detection with direct double focusing inductively coupled plasma mass spectrometric measurements for ultratrace multi-element determinations in sea-water," *Anal. Chim. Acta* 429(2), 227-235. DOI: 10.1016/S0003-2670(00)01297-6

Ferreira, S. L. C., Korn, M. G. A., Ferreira, H. S., Da Silva, E. G. P., Araujo, R. G. O., Souza, A. S., Macedo, S. M., Lima, D. D. C., De Jesus, R. M., Amorim, F. A. C., *et*

al. (2007). "Application of multivariate techniques in optimization of spectroanalytical methods," *Appl. Spectrosc. Rev*. 42(5), 475-491. DOI: 10.1080/05704920701551506

Ferreira, S. L. C., Queiroz, A. S., Quorn, M. D. A., and Costa, A. C. S. (1997). "Determination of nickel in alkaline salts by inductively coupled plasma atomic emission spectroscopy using 1-(2-thiazolylazo)-*p*-cresol for preconcentration and separation," *Anal. Lett*. 30(12), 2251-2260. DOI: 10.1080/00032719708001736

Fliegel, D., Frei, C., Fontaine, G., Hu, Z. C., Gao, S., and Günther, D. (2011). "Sensitivity improvement in laser ablation inductively coupled plasma mass spectrometry achieved using a methane/argon and methanol/water/argon mixed gas plasma," *Analyst* 136(23), 4925-4934. DOI: 10.1039/c0an00953a

Folgar, S., Torres, E., Pérez-Rama, M., Cid, A., Herrero, C., and Abalde, J. (2009). "*Dunaliella salina* as marine microalga highly tolerant to but a poor remover of cadmium," *J. Hazard. Mater*. 165, 486-493. DOI: 10.1016/j.jhazmat.2008.10.010

Gadd, G. M., and White, C. (1993). "Microbial treatment of metal pollution - A working biotechnology?," *Trends Biotechnol*. 11(8), 353-359. DOI: 10.1016/0167-7799(93)90158-6

Garnham, G. W. (1997). *The Use of Algae as Metal Biosorbents*, CRC Press, London, UK.

Gellerstedt, F., Wagberg, L., and Gatenholm, P. (2000). "Swelling behavior of succinylated fibers," *Cellulose* 7(1), 67-86.

Gonzálvez, A., Armenta, S., Pastor, A., and De la Guardia, M. (2008). "Searching the most appropriate sample pretreatment for the elemental analysis of wines by inductively coupled plasma-based techniques," *J. Agr. Food Chem*. 56(13), 4943-4954. DOI: 10.1021/jf800286y

Granholm, K., Harju, L., and Ivaska, A. (2010). "Desorption of metal ions from kraft pulps. Part 1. Chelation of hardwood and softwood kraft pulp with EDTA," *BioResources* 5(1), 206-226. DOI: 10.15376/biores.5.1.206-226

Grégoire, D. C. (2000). "Electrothermal vaporisation sample introduction for ICP MS," in: *Discrete Sample Introduction Techniques for Inductively Coupled Plasma Mass Spectrometry*, D. Beauchemin, C. D. Grégoire, D. Günther, V. Karanassios, J.-M. Mermet, and T. J. Wood (eds.), Elsevier, Amsterdam, Netherlands, pp. 347.

Grinberg, P., Yang, L., Mester, Z., Willie, S., and Sturgeon, R. E. (2006). "Comparison of laser ablation, electrothermal vaporization and solution nebulization for the determination of radionuclides in liquid samples by inductively coupled plasma mass spectrometry," *J. Anal. Atom. Spectrom*. 21(11), 1202-1208. DOI: 10.1039/B607911C

Grotti, M., Terol, A., and Todolí, J. L. (2014). "Speciation analysis by small-bore HPLC coupled to ICP-MS," *TrAC-Trend. Anal. Chem*. 61, 92-106. DOI: 10.1016/j.trac.2014.06.009

Günther, D., and Mermet, J.-M. (2000). *Discrete Sample Introduction Techniques for Inductively Coupled Plasma Mass Spectrometry*, Elsevier, Amsterdam, Netherlands.

Guerquin-Kern, J.-L., Wu, T.-D., Quintana, C., and Croisy, A. (2005). "Progress in analytical imaging of the cell by dynamic secondary ion mass spectrometry (SIMS microscopy)," *Biochim. Biophys. Acta* 1724(3), 228-238. DOI:10.1016/j.bbagen.2005.05.013

Gupta, R., Ahuja, P., Khan, S., Saxena, R. K., and Mohapatra, H. (2000). "Microbial biosorbents: Meeting challenges of heavy metal pollution in aqueous solutions," *Curr. Sci. India* 78(8), 967-973.

Han, Y., Boateng, A. A., Qi, P. X., Lima, I. M., and Chang, J. (2013). "Heavy metal and phenol adsorptive properties of biochars from pyrolyzed switchgrass and woody biomass in correlation with surface properties," *J. Environ. Manage.* 118, 196-204. DOI: 10.1016/j.jenvman.2013.01.001

Harder, M. L., and Einspehr, D. W. (1980). "Levels of some essential metals in bark," *Tappi* 63(2), 110.

Hashem, A., Abou-Okeil, A., El-Shafie, A., and El-Sakhawy, M. (2006a). "Grafting of high-cellulose pulp extracted from sunflower stalks for removal of Hg (II) from aqueous solution," *Polym.-Plast. Technol.* 45(1), 135-141. DOI: 10.1080/03602550500373790

Hashem, A., Aly, A. A., Aly, A. S., and Hebeish, A. (2006b). "Quaternization of cotton stalks and palm tree particles for removal of acid dye from aqueous solutions," *Polym.-Plast. Technol.* 45(3), 389-394. DOI: 10.1080/03602550600553689

Haupt, K. (2001). "Molecularly imprinted polymers in analytical chemistry," *Analyst* 126(6), 747-756. DOI: 10.1039/B102799A

Hawkes, J. S. (1997). "What is a "heavy metal"?," *J. Chem. Educ.* 74(11), 1369-1374. DOI: 10.1021/ed074p1374

Heinrich, C. A. (2006). "From fluid inclusion microanalysis to large-scale hydrothermal mass transfer in the Earth's interior," *J. Miner. Petrol. Sci.* 101(3), 110-117. DOI: 10.2465/jmps.101.110

Heitmar, E. M., Hinners, T. A., Rowan, J. T., and Riviello, J. M. (1990). "Minimization of interferences in inductively coupled plasma mass spectrometry using on-line preconcentration," *Anal. Chem.* 62(8), 857-864. DOI: 10.1021/ac00207a018

Herawati, N., Suzuki, S., Hayashi, K., Rivai, I. F., and Koyoma, H. (2000). "Cadmium, copper and zinc levels in rice and soil of Japan, Indonesia and China by soil type," *B. Environ. Contam. Tox.* 64(1), 33-39. DOI: 10.1007/s001289910006

Hernández, P. P., Moreno, V., Olivari, F. A., and Allende, M. L. (2006). "Sub-lethal concentrations of waterborne copper are toxic to lateral line neuromasts in zebrafish (*Danio rerio*)," *Hearing Res.* 213(1-2), 1-10. DOI: 10.1016/j.heares.2005.10.015

Heumann, K. G. (1992). "Isotope dilution mass spectrometry (IDMS) of the elements," *Mass Spectrom. Rev.* 11(1), 41-67. DOI: 10.1016/0165-9936(82)88024-2

Hirner, A. V., and Emons, H. (2004). *Organic Metal and Metalloid Species in the Environment*, A. V. Hirner and H. Emons (eds.), Springer, Berlin, Germany.

Hokkanen, S., Repo, E., and Sillanpää, M. (2013). "Removal of heavy metals from aqueous solutions by succinic anhydride modified mercerized nanocellulose," *Chem. Eng. J.* 223, 40-47. DOI: 10.1016/j.cej.2013.02.054

Hon, D. N.-S., and Shirashi, N. (1991). *Wood and Cellulosic Chemistry*, Marcel Dekker, Inc., New York, USA.

Houk, R. S., and Praphairaksit, N. (2001). "Dissociation of polyatomic ions in the inductively coupled plasma," *Spectrochim. Acta. B* 56(7), 1069-1096. DOI: 10.1016/S0584-8547(01)00236-1

Hu, B., Yu, S.-H., Wang, K., Liu, L., and Xu, X.-W. (2008). "Functional carbonaceous materials from hydrothermal carbonization of biomass: An effective chemical process," *Dalton T.* 40, 5414-5423. DOI: 10.1039/b804644c

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. DOI: 10.15376/biores.6.2.Hubbe

Hung, D. Q., Nekrassova, O., and Compton, R. G. (2004). "Analytical methods for inorganic arsenic in water: A review," *Talanta* 64(2), 269-277. DOI: 10.1016/j.talanta.2004.01.027

Hwang, I. H., Nakajima, D., Matsuto, T., and Sugimoto, T. (2008). "Improving the quality of waste-derived char by removing ash," *Waste Manage*. 28(2), 424-434. DOI: 10.1016/j.wasman.2006.11.015

Iglesias, M., Besalu, E., and Antico, E. (2007). "Internal standardization atomic spectrometry and geographical pattern recognition techniques for the multielement analysis and classification of catalonian red wines," *J. Agr. Food Chem*. 55, 219-225. DOI: 10.1021/jf0629585

Inyang, M. D., Gao, B., Ding, W., Pullammanappallil, P., Zimmerman, A. R., and Cao, X. (2011). "Enhanced lead sorption by biochar derived from anaerobically digested sugarcane bagasse," *Sep. Sci. Technol*. 46(12), 1950-1956. DOI: 10.1080/01496395.2011.584604

Inyang, M. D., Gao, B., Yao, Y., Xue, Y., Zimmerman, A. R., Pullammanappallil, P., and Cao, X. (2012). "Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass," *Bioresource Technol*. 110, 50-56. DOI: 10.1016/j.biortech.2012.01.072

Inyang, M. D., Gao, B., Zimmerman, A., Zhou, Y., and Cao, X. (2015). "Sorption and cosorption of lead and sulfapyridine on carbon nanotube-modified biochars," *Environ. Sci. Pollut. R*. 22(3), 1868-1876. DOI: 10.1007/s11356-014-2740-z

Inyang, M. I., Gao, B., Yao, Y., Xue, Y., Zimmerman, A., Mosa, A., Pullammanappallil, P., Ok, Y. S., and Cao, X. (2016). "A review of biochar as a low-cost adsorbent for aqueous heavy metal removal," *Crit. Rev. Environ. Sci. Tec*. 46(4), 406-433. doi.org/10.1080/10643389.2015.1096880

Ioannidou, O., and Zabaniotou, A. (2007). "Agricultural residues as precursors for activated carbon production – A review," *Renew. Sust. Energ. Rev*. 11(9), 1966-2005. DOI: 10.1016/j.rser.2006.03.013

Isogai, A., and Kato, Y. (1998). "Preparation of polyuronic acid from cellulose by TEMPO-mediated oxidation," *Cellulose* 5(3), 153-164. DOI: 10.1023/A:1009208603673

Jackson, B. P., and Bertsch, P. M. (2001). "Determination of arsenic speciation in poultry wastes by IC-ICP-MS," *Environ. Sci. Technol*. 35(24), 4868-4873. DOI: 10.1021/es0107172

Jakubowski, N., and Stuever, D. (1997). *New Instrumental Developments and Analytical Applications in ICP-MS in Plasma Source Mass Spectrometry: Developments and Applications*, The Royal Society of Chemistry, Cambridge, England.

Jang, A., Seo, Y., and Bishop, P. L. (2005). "The removal of heavy metals in urban runoff by sorption on mulch," *Environ. Pollut*. 133(1), 117-127. DOI: 10.1016/j.envpol.2004.05.020

Järup, L. (2003). "Hazards of heavy metal contamination," *Brit. Med. Bull*. 68(1), 167-182. DOI: 10.1093/bmb/ldg032

Jiang, N., Chang, X. J., Zheng, H., He, Q., and Hu, Z. (2006). "Selective solid-phase extraction of nickel(II) using a surface-imprinted silica gel sorbent," *Anal. Chim. Acta* 577(2), 225-231. DOI: 10.1016/j.aca.2006.06.049

Johns, M. M., Marshall, W. E., and Toles, C. A. (1998). "Agricultural by-products as granular activated carbons for adsorbing dissolved metals and organics," *J. Chem. Technol. Biot*. 71(2), 131-140. DOI: 10.1002/(SICI)1097-4660(199802)71:2<131::AID-JCTB821>3.0.CO;2-K

Jyske, T., Mäkinen, H., Kalliokoski, T., and Nöjd, P. (2014). "Intra-annual tracheid production of Norway spruce and Scots pine across a latitudinal gradient in Finland," *Agr. Forest Meteorol*. 194, 241-254. DOI: 10.1016/j.agrformet.2014.04.015

Keiluweit, M., and Kleber, M. (2009). "Molecular-level interactions in soils and sediments: The role of aromatic Π-systems," *Environ. Sci. Technol*. 43(10), 3421-3429. DOI: 10.1021/es8033044

Khan, A., Jong, W., Jansens, P., and Spliethoff, H. (2009). "Biomass combustion in fluidized bed boilers: Potential problems and remedies," *Fuel Process Technol*. 90(1), 21-50. DOI: 10.1016/j.fuproc.2008.07.012

Khan, U., and Rao, R. A. K. (2017). "A high activity adsorbent of chemically modified *Cucurbita moschata* (a novel adsorbent) for the removal of Cu(II) and Ni(II) from aqueous solution: Synthesis, characterization and metal removal efficiency," *Proc. Safe. Environ. Protect*. 107, 238-258. DOI: 10.1016/j.psep.2017.02.008

Kinoshita, C. M. (1991). "Cogeneration in the Hawaiian sugar industry," *Bioresource Technol*. 35(3), 231-237. DOI: 10.1016/0960-8524(91)90119-5

Kment, P., Mihaljevĭ, M., Ettler, V., Sěbek, O., Strnad, L., and Rohlová, L. (2005). "Differentiation of Czech wines using multielement composition - A comparison with vineyard soil," *Food Chem*. 91(1), 157-165. DOI: 10.1016/j.foodchem.2004.06.010

Kokšal, J., Synek, V., and Janos, P. (2002). "Extraction-spectrometric determination of lead in high-purity aluminium salts," *Talanta* 58(2), 325-330. DOI: 10.1016/S0039-9140(02)00247-3

Koljonen, K., Mustranta, A., and Stenius, P. (2004). "Surface characterisation of mechanical pulps by polyelectrolyte adsorption," *Nord. Pulp. Pap. Res. J*. 19(4), 495-505.

Konn, J., Pranovich, A., Fardim, P., and Holmbom, B. (2007). "Characterisation and effects of new anionic groups formed during chemithermomechanical pulping of spruce," *Colloid. Surface. A*. 296(1-3), 1-7. DOI: 10.1016/j.colsurfa.2006.09.047

Kookana, R. S. (2010). "The role of biochar in modifying the environmental fate, bioavailability, and efficacy of pesticides in soils: A review," *Aust. J. Soil Res*. 48(6-7), 627-637. DOI: 10.1071/SR10007

Kumar, N., Bansal, A., Sarma, G. S., and Rawal, R. K. (2014). "Chemometrics tools used in analytical chemistry: An overview," *Talanta* 123, 186-199. DOI: 10.1016/j.talanta.2014.02.003

Kumar, S., Loganathan, V. A., Gupta, R. B., and Barnett, M. O. (2011). "An assessment of U(VI) removal from groundwater using biochar produced from hydrothermal carbonization," *J. Environ. Manage*. 92(10), 2504-2512. DOI: 10.1016/j.jenvman.2011.05.013

Laine, J., Buchert, J., Viikari, L., and Stenius, P. (1996). "Characterization of unbleached kraft pulps by enzymic treatment, potentiometric titration and polyelectrolyte adsorption," *Holzforschung* 50(3), 208-214. DOI: 10.1515/hfsg.1996.50.3.208

Lambert, M. J. (1981). "Research note no. 45: Inorganic constituents in wood and bark of new south Wales forest tree species," Forestry Commission N. S. W., Sydney, Australia.

bioresources.com

Lattao, C., Cao, X., Mao, J., Schmidt-Rohr, K., and Pignatello, J. J. (2014). "Influence of molecular structure and adsorbent properties on sorption of organic compounds to a temperature series of wood chars," *Environ. Sci. Technol*. 48(9), 4790-4798. DOI: 10.1021/es405096q

Laureysens, I., Blust, R., De Temmerman, L., Lemmens, C., and Ceulemans, R. (2004). "Clonal variation in heavy metal accumulation and biomass production in a poplar coppice culture: I. Seasonal variation in leaf, wood and bark concentrations," *Environ. Pollut*. 131(3), 485-494. DOI: 10.1016/j.envpol.2004.02.009

Lehmann, J. (2007). "Bio-energy in the black," *Front. Ecol. Environ*. 5(7), 381-387. DOI: 10.1890/1540-9295(2007)5[381:BITB]2.0.CO;2

Li, H., Li, Z., Liu, T., Xiao, X., Peng, Z., and Deng, L. (2008). "A novel technology for biosorption and recovery hexavalent chromium in wastewater by bio-functional magnetic beads," *Bioresource Technol*. 99(14), 6271-6279. DOI: 10.1016/j.biortech.2007.12.002

Li, J. T., Qiu, J. W., Wang, X. W., Zhong, Y., Lan, C. Y., and Shu, W. S. (2006). "Cadmium contamination in orchard soils and fruit trees and its potential health risk in Guangzhou, China," *Environ. Pollut*. 143(1), 159-165. DOI: 10.1016/j.envpol.2005.10.016

Li, L., and Zhang, H. X. (2004). "Preparing levoglucosan derived from waste material by pyrolysis," *Energ. Source*. 26(11), 1053-1059. DOI: 10.1080/00908310490494559

Liao, C.-M., Ju, Y.-R., Chen, W.-Y., and Chen, B.-C. (2011). "Assessing the impact of waterborne and diet borne cadmium toxicity on susceptibility risk for rainbow trout," *Sci. Total Environ*. 409(3), 503-513. DOI: 10.1016/j.scitotenv.2010.10.044

Lindström, T. (1992). "Chemical factors affecting the behaviour of fibres during papermaking," *Nord. Pulp. Pap. Res. J*. 7(4), 181-192. DOI: 10.3183/NPPRJ-1992-07-04-p181-192

Liu, Z., and Zhang, F.-S. (2009). "Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass," *J. Hazard. Mater*. 167(1-3), 933-939. DOI: 10.1016/j.jhazmat.2009.01.085

Lobiński, R., Schaumlöffel, D., and Szpunar, J. (2006). "Mass spectrometry in bioinorganic analytical chemistry," *Mass Spectrom. Rev*. 25(2), 255-289. DOI: 10.1002/mas.20069

Lopičić, Z. R., Stojanović, M. D., Kaluđerović Radoičić, T. S., Milojković, J. V., Petrović, M. S., Mihajlović, M. L., and Kijevčanin, M. L. J. (2017). "Optimization of the process of Cu(II) sorption by mechanically treated *Prunus persica* L. – Contribution to sustainability in food processing industry," *J. Clean. Prod*. 156, 95-105. DOI: 10.1016/j.jclepro.2017.04.041

Low, K. S., Lee, C. K., and Mak, S. M. (2004). "Sorption of copper and lead by citric acid modified wood," *Wood Sci. Technol*. 38(8), 629-640. DOI: 10.1007/s00226-003-0201-9

Lu, H., Mou, S., Yan, Y., Tong, S., and Riviello, J. M. (1998). "On-line pretreatment and determination of Pb, Cu and Cd at the $\mu g \, l^{-1}$ level in drinking water by chelation ion chromatography," *J. Chromatogr. A* 800(2), 247-255. DOI: 10.1016/S0021-9673(97)01127-8

Madrid, Y., and Cámara, C. (1997). "Biological substrates for metal preconcentration and speciation," *TrAC-Trend. Anal. Chem*. 16(1), 36-44. DOI: 10.1016/S0165-9936(96)00075-1

Mager, E. M. (2011). *Lead of the Fish Physiology*, Academic Press, Elsevier, Inc., NewYork, USA.

Mahar, A., Wang, P., Ali, A., Awasthi, M. K., Lahori, A. H., Wang, Q., Li, R., and Zhang, Z. (2016). "Challenges and opportunities in the phytoremediation of heavy metals contaminated soils: A review," *Ecotox. Environ. Safe*. 126, 111-121. DOI: 10.1016/j.ecoenv.2015.12.023

Mahmood, T., and Islam, K. R. (2006). "Response of rice seedlings to copper toxicity and acidity," *J. Plant Nutr*. 29(5), 943-957. DOI: 10.1080/01904160600651704

Mahmoud, M. E., Osman, M. M., Ahmed, S. B., and Abdel-Fattah, T. M. (2012). "Enhanced removal of lead by chemically and biologically treated carbonaceous materials," *Sci. World J*. Article ID 604198, 1-11. DOI: 10.1100/2012/604198

Maekawa, E., and Koshijima, T. (1990). "Preparation and characterisation of hydroxamic acid derivatives and its metal complexes derived from cellulose," *J. Appl. Polym. Sci*. 40(9-10), 1601-1613. DOI: 10.1002/app.1990.070400916

Majumdar, S., Peralta-Videa, J. R., Castillo-Michel, H., Hong, J., Rico, C. M., and Gardea-Torresdey, J. L. (2012). "Applications of synchrotron mu-XRF to study the distribution of biologically important elements in different environmental matrices: A review," *Anal. Chim. Acta* 755, 1-16. DOI: 10.1016/j.aca.2012.09.050

Malik, A. (2004). "Metal bioremediation through growing cells," *Environ. Int*. 30(2), 261-278. DOI: 10.1016/j.envint.2003.08.001

March, R. E., and Todd, J. F. J. (1995). "Practical aspects of ion trap mass spectrometry," in: *Modern Mass Spectrometry Series*, CRC press, Boca Raton, FL, pp. 448.

Marin, B., Valladon, M., Polve, M., and Monaco, A. (1997). "Reproducibility testing of a sequential extraction scheme for the determination of trace metal speciation in a marine reference sediment by inductively coupled plasma-mass spectrometry," *Anal. Chim. Acta* 342(2-3), 91-112. DOI: 10.1016/S0003-2670(96)00580-6

Marisa, C., Almeida, R., Tiresa, M., and Vasconcelos, S. D. (1999). "Determination of lead isotope ratios in port wine by inductively coupled plasma mass spectrometry after pre-treatment by UV-irradiation," *Anal. Chim. Acta* 396(1), 45-53. DOI: 10.1016/S0003-2670(99)00356-6

Marisa, C., Almeida, R., and Vasconcelos, M. T. S. D. (2003). "Multielement composition of wines and their precursors including provenance soil and their potentialities as fingerprints of wine origin," *J. Agr. Food. Chem*. 51(16), 4788-4798. DOI: 10.1021/jf034145b

Mata, Y. N., Blázquez, M. L., Ballester, A., González, F., and Muñoz, J. A. (2009). "Sugar-beet pulp pectin gels as biosorbent for heavy metals: Preparation and determination of biosorption and desorption characteristics," *Chem. Eng. J*. 150(2-3), 289-301. DOI: 10.1016/j.cej.2009.01.001

McGeer, J. C., Niyogi, S., and Smith, S. D., (2011). *Cadmium of the Fish Physiology*, Academic Press, Elsevier, Inc., New York, USA.

Memon, J. R., Memon, S. Q., Bhanger, M. I., Memon, G. Z., El-Turki, A., and Allen, G. C. (2008). "Characterization of banana peel by scanning electron microscopy and FT-IR spectroscopy and its use for cadmium removal," *Colloid. Surface. B* 66(2), 260-265. DOI: 10.1016/j.colsurfb.2008.07.001

Medellin-Castillo, N. A., Padilla-Ortega, E., Regules-Martínez, M. C., Leyva-Ramos, R., Ocampo-Pérez, R., and Carranza-Alvarez, C. (2017). "Single and competitive adsorption of Cd(II) and Pb(II) ions from aqueous solutions onto industrial chili seeds

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(*Capsicum annuum*) waste," *Sustain. Environ. Res*. 27(2), 61-69. DOI: 10.1016/j.serj.2017.01.004

Meunier, N., Blais, J. F., and Tyagi, R. D. (2004). "Removal of heavy metals from acid soil leachate using cocoa shells in a batch counter-current sorption process," *Hydrometallurgy* 73(3-4), 225-235. DOI: 10.1016/j.hydromet.2003.10.011

Michalke, B. (2002a). "The coupling of LC to ICP-MS in element speciation: I. General aspects," *TrAC-Trend. Anal. Chem*. 21(3), 142-153. DOI: 10.1016/S0165-9936(01)00146-7

Michalke, B. (2002b). "The coupling of LC to ICP-MS in element speciation – Part II: Recent trends in application," *TrAC-Trend. Anal. Chem*. 21(3), 154-165. DOI: 10.1016/S0165-9936(02)00303-5

Minami, T., Konagaya, W., Zheng, L., Takano, S., Sasaki, M., Murata, R., Nakaguchi, Y., and Sohrin, Y. (2015). "An off-line automated preconcentration system with ethylenediaminetriacetate chelating resin for the determination of trace metals in seawater by high-resolution inductively coupled plasma mass spectrometry," *Anal. Chim. Acta* 854, 183-190. DOI: 10.1016/j.aca.2014.11.016

Mirzaei, M., Behzadi, M., Abadi, N. M., and Beizaei, A. (2011). "Simultaneous separation/preconcentration of ultra trace heavy metals in industrial wastewaters by dispersive liquid–liquid microextraction based on solidification of floating organic drop prior to determination by graphite furnace atomic absorption spectrometry," *J. Hazard. Mater*. 186(2-3), 1739-1743. DOI: 10.1016/j.jhazmat.2010.12.080

Miyazaki, A., and Reimer, R. A. (1993). "Determination of lead isotope ratios and concentrations in sea-water by inductively coupled plasma mass spectrometry after preconcentration using Chelex-100," *J. Anal. Atom. Spectrom*. 8(3), 449-452. DOI: 10.1039/JA9930800449

Mohan, D., Pittman, C. U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P. H., Alexandre-Franco, M. F., Gómez-Serrano, V., and Gong, H. (2007). "Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production," *J. Colloid Interf. Sci*. 310(1), 57-73. DOI: 10.1016/j.jcis.2007.01.020

Mohan, D., Sarswat, A., Ok, Y., and Pittman, Jr., C. U. (2014). "Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent: A critical review," *Bioresource Technol*. 160, 191-202. DOI: 10.1016/j.biortech.2014.01.120

Mohan, D., Singh, K. P., and Singh, V. K. (2006). "Chromium (III) removal from wastewater using low cost activated carbon derived from agriculture waste material and activated carbon fabric cloth," *J. Hazard. Mater*. 135(1-3), 280-295. DOI: 10.1016/j.jhazmat.2005.11.075

Moldovan, M., Krupp, E. M., Holliday, A. E., and Donard, O. F. X. (2004). "High resolution sector field ICP-MS and multicollector ICP-MS as tools for trace metal speciation in environmental studies: A review," *J. Anal. Atom. Spectrom*. 19(7), 815-940. DOI: 10.1039/b403128h

Monni, S., Salemaa, M., and Millar, N. (2000). "The tolerance of *Empetrum nigrum* to copper and nickel," *Environ. Pollut*. 109(2), 221-229. DOI: 10.1016/S0269-7491(99)00264-X

Montes-Atenas, G., and Schroeder, S. L. M. (2015). "Sustainable natural adsorbents for heavy metal removal from wastewater: Lead sorption on pine bark (*Pinus radiata* D.Don)," *Surf. Interface Anal*. 47(10), 996-1000. DOI: 10.1002/sia.5807

Moore, J. W., and Ramamoorthy, S. (1984). *Heavy Metals in Natural Waters*, Springer-Verlag, New York, USA.

Moreno, I. M., González-Weller, D., Gutierrez, V., Marino, M., Cameán, A. M., Gustavo González, A., and Hardisson, A. (2007). "Differentiation of two canary DO red wines according to their metal content from inductively coupled plasma optical emission spectrometry and graphite furnace atomic absorption spectrometry by using Probabilistic Neutral Networks," *Talanta* 72(1), 263-268. DOI: 10.1016/j.talanta.2006.10.029

Mukherjee, A., Zimmerman, A. R., and Harris, W. (2011). "Surface chemistry variations among a series of laboratory-produced biochars," *Geoderma* 163(3-4), 247-255. DOI: 10.1016/j.geoderma.2011.04.021

Na, J., Chang, X. J., Hong, Z., Qun, H., and Zheng, H. (2006). "Selective solid-phase extraction of nickel(II) using a surface-imprinted silica gel sorbent," *Anal. Chim. Acta* 577(2), 225-231. DOI: 10.1016/j.aca.2006.06.049

Nagajyoti, P. C., Lee, K. D., and Sreekanth, T. V. M. (2010). "Heavy metals, occurrence and toxicity for plants: A review," *Environ. Chem. Lett*. 8(3), 199-216. DOI: 10.1007/s10311-010-0297-8

Nakazato, T., Tao, H., Taniguchi, T., and Isshiki, K. (2002). "Determination of arsenite, arsenate, and monomethylarsonic acid in seawater by ion-exclusion chromatography combined with inductively coupled plasma mass spectrometry using reaction cell and hydride generation techniques," *Talanta* 58(1), 121-132. DOI: 10.1016/S0039-9140(02)00261-8

Nakicenovic, N., and Swart, R. (2000). "Special report on emission scenarios," in: *InterGovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, England, pp. 599.

Navarro, R. R., Sumi, K., Fujii, N., and Matsumura, M. (1996). "Mercury removal from wastewater using porous cellulose carrier modified with polyethyleneimine," *Water Res*. 30(10), 2488-2494. DOI: 10.1016/0043-1354(96)00143-1

Navarro, R. R., Tatsumi, K., Sumi, K., and Matsumura, M. (2001). "Role of anions on heavy metal sorption of a cellulose modified with poly(glycidylmethacrylate) and polyethyleneimine," *Water Res*. 35(11), 2724-2730. DOI: 10.1016/S0043-1354(00)00546-7

Nelms, S. (2005). *Inductively Coupled Plasma Mass Spectrometry Handbook*, Blackwell, Carlton, Australia.

Nicolaï, M., Rosin, C., Tousset, N., and Nicolai, Y. (1999). "Trace metals analysis in estuarine and seawater by ICP-MS using on line preconcentration and matrix elimination with chelating resin," *Talanta* 50(2), 433-444. DOI: 10.1016/S0039-9140(99)00130-7

Nielsen, H. P., Frandsen, F. J., Dam-Johansen, K., and Baxter, L. L. (2000). "The implications of chlorine-associated corrosion on the operation of biomass-fired boilers," *Prog. Energ. Combust.* 26(3), 283-298. DOI: 10.1016/S0360-1285(00)00003-4

Nölte, J. (2000). "Trinkwasser analyse per ICP-OES/ Ultraschallzerstaubung [Analysis of drinking water with ICP-OES/ultrasound atomization]," *Labor Praxis* 24(7-8), 30-32.

Novaes, C. G., Bezerra, M. A., Paranhos da Silva, E. G., Pinto dos Santos, A. M., Da Silva Romão, I. L., and Neto, J. H. H. (2016). "A review of multivariate designs applied to the optimization of methods based on inductively coupled plasma optical

emission spectrometry (ICP OES)," *Microchem. J*. 128, 331-346. DOI: 10.1016/j.microc.2016.05.015

Nuhoglu, Y., and Oguz, E. (2003). "Removal of copper (II) from aqueous solutions by biosorption on the cone biomass of *Thuja orientalis*," *Process Biochem.* 38(11), 1627-1631. DOI: 10.1016/S0032-9592(03)00055-4

O'Connell, D. W., Birkinshaw, C., and O'Dwyer, T. F. (2008). "Heavy metal adsorbents prepared from the modification of cellulose: A review," *Bioresource Technol*. 99(15), 6709-6724. DOI: 10.1016/j.biortech.2008.01.036

Özdemir, S., Okumus, V., Kılınc, E., Bilgetekin, H., Dündar, A., and Ziyadanogˇullari, B. (2012). "Pleurotus eryngii immobilized Amberlite XAD-16 as a solid-phase biosorbent for preconcentrations of Cd^{2+} and Co^{2+} and their determination by ICP-OES," *Talanta* 99, 502-506. DOI: 10.1016/j.talanta.2012.06.017

Pagliuca, A., and Mufti, G. J. (1990). "Lead poisoning: An age-old problem," *BMJ-Brit. Med. J.* 300(6728), 830. DOI: 10.1136/bmj.300.6728.830

Pagnanelli, F., Esposito, A., Toro, L., and Veglio, F. (2003). "Metal speciation and pH effect on Pb, Cu, Zn and Cd biosorption onto *Sphaerotilus natans*: Langmuir-type empirical model," *Water Res*. 37(3), 627-633. DOI: 10.1016/S0043-1354(02)00358-5

Palma, G., Freer, J., and Baeza, J. (2003). "Removal of metal ions by modified *Pinus radiata* bark and tannins from water solutions," *Water Res*. 37(20), 4974-4980. DOI: 10.1016/j.watres.2003.08.008

Paradelo, R., and Barral, M. T. (2012). "Evaluation of the potential capacity as biosorbents of two MSW composts with different Cu, Pb and Zn concentrations," *Bioresource Technol*. 104, 810-813. DOI: 10.1016/j.biortech.2011.11.012

Park, D., Yun, Y.-S., and Park, J. M. (2010). "The past, present, and future trends of bio-sorption," *Biotechnol. Bioproc. E*. 15(1), 86-102. DOI: 10.1007/s12257-009-0199-4

Patterson, J. W. (1985). *Industrial Wastewater Treatment Technology*, Butterworth Publisher, Stoneham, USA.

Perat, C., and Ni, Y. (2001). "UV-Vis spectra of lignin model compounds in the presence of meal ions and chelants," *J. Wood Chem. Technol*. 21(2), 113-125. DOI: 10.1081/WCT-100104222

Pesavento, M., and Biesuz, R. (1997). "Sorption of divalent metal ions on a iminodiacetic resin from artificial seawater," *Anal. Chim. Acta* 346(3), 381-391. DOI: 10.1016/S0003-2670(97)90083-0

Pettersen, R. C. (1984). "The chemical composition of wood," in: *The Chemistry of Solid Wood, Advances in Chemistry*, Volume 207, R. M. Rowell (ed.), American Chemical Society, Washington D.C., USA, pp. 57-126.

Poole, C. F. (2003). "New trends in solid-phase extraction," *TrAC-Trend. Anal. Chem*. 22(6), 362-373. DOI: 10.1016/S0165-9936(03)00605-8

Prohaska, T., Stadlbauer, C., Wimmer, R., Stingeder, G., Latkoczy, C., Hoffmann, E., and Stephanowitz, H. (1998). "Investigation of element variability in tree rings of young Norway spruce by laser-ablation-ICPMS," *Sci. Total Environ*. 219(1), 29-39. DOI: 10.1016/S0048-9697(98)00224-1

Pu, X. L., Hu, B., Jiang, Z. C., and Huang, C. Z. (2005). "Speciation of dissolved iron (II) and iron (III) in environmental water samples by gallic acid-modified nanometer-sized alumina micro-column separation and ICP-MS determination," *Analyst* 130(8), 1175-1181. DOI: 10.1039/b502548f

Qaiser, S., Saleemi, A. R., and Ahmad, M. M. (2007). "Heavy metal uptake by agro based waste materials," *Electron. J. Biotechn*. 10(3), 409-416. DOI: 10.2225/vol10-issue3-fulltext-12

Rahmi, D., Zhu, Y., Fujimori, E., Umemura, T., and Haraguchi, H. (2007). "Multielement determination of trace metals in seawater by ICP-MS with aid of down-sized chelating resin-packed minicolumn for preconcentration," *Talanta* 72(2), 600-606. DOI: 10.1016/j.talanta.2006.11.023

Raji, C., Shubha, K. P., and Anirudhan, T. S. (1997). "Use of chemically modified sawdust in the removal of Pb (II) ions from aqueous media," *Indian Journal of Environmental Health* 39, 230-238.

Rao, T. P., Daniel, S., and Gladis, J. M. (2004). "Tailored materials for preconcentration or separation of metals by ion-imprinted polymers for solid-phase extraction (IIP-SPE)," *TrAC-Trend. Anal. Chem*. 23(1), 28-35. DOI: 10.1016/S0165-9936(04)00106-2

Rattanachongkiat, S., Millwarda, G. E., and Foulkes, M. E. (2004). "Determination of arsenic species in fish, crustacean and sediment samples from Thailand using high performance liquid chromatography (HPLC) coupled with inductively coupled plasma mass spectrometry (ICP-MS)," *J. Environ. Monitor*. 6(4), 254-261. DOI: 10.1039/b312956j

Ray, S. J., Andrade, F., Gamez, G., McClenathan, D., Rogers, D., Schilling, G., Wetzel, W., and Hieftje, G. M. (2004). "Plasma-source mass spectrometry for speciation analysis: State-of-the-art," *J. Chromatogr. A* 1050(1), 3-34. DOI: 10.1016/S0021-9673(04)01309-3

Reddad, Z., Gerente, C., Andres, Y., and LeCloirec, P. (2002a). "Adsorption of several metal ions onto a low-cost biosorbent: Kinetic and equilibrium studies," *Environ. Sci. Technol*. 36(9), 2067-2073. DOI: 10.1021/es0102989

Reddad, Z., Gerente, C., Andres, Y., Ralet, M.-C., Thibault, J.-F., and Cloirec, P. L. (2002b). "Ni (II) and Cu (II) binding properties of native and modified sugar beet pulp," *Carbohyd. Polym*. 49(1), 23-31. DOI: 10.1016/S0144-8617(01)00301-0

Regmi, P., Garcia Moscoso, J. L., Kumar, S., Cao, X., Mao, J., and Schafran, G. (2012). "Removal of copper and cadmium from aqueous solution using switchgrass biochar produced *via* hydrothermal carbonization process," *J. Environ. Manage*. 109, 61-69. DOI: 10.1016/j.jenvman.2012.04.047

Reimann, C., Arnoldussen, A., Englmaier, P., Filzmoser, P., Finne, T. E., Garrett, R. G., Koller, F., and Nordgulen, Ø. (2007). "Element concentrations and variations along a 120 km long transect in south Norway - anthropogenic *vs*. geogenic *vs*. biogenic element sources and cycles," *Appl. Geochem*. 22(4), 851-871. DOI: 10.1016/j.apgeochem.2006.12.019

Reimann, C., Ottesen, R. T., Andersson, M., Arnoldussen, A., Koller, F., and Englmaier, P. (2008). "Element levels in birch and spruce wood ashes - green energy?," *Sci. Total Environ*. 393(2-3), 191-197. DOI: 10.1016/j.scitotenv.2008.01.015

Rhee, S.-W., and Park, H.-S. (2010). "Effect of mixing ratio of woody waste and food waste on the characteristics of carbonization residue," *J. Mater. Cycles. Waste Manage*. 12(3), 220-226. DOI: 10.1007/s10163-010-0291-z

Riley, J. P., and Taylor, D. (1968). "Chelating resins for the concentration of trace elements from sea water and their analytical use in conjunction with atomic absorption spectrophotometry," *Anal. Chim. Acta* 40, 479-485. DOI: 10.1016/S0003-2670(00)86764-1

Roig-Navarro, A. F., Martinez-Bravo, Y., López, F. J., and Hernández, F. (2001). "Simultaneous determination of arsenic species and chromium(VI) by high-performance liquid chromatography–inductively coupled plasma-mass spectrometry," *J. Chromatogr. A* 912(2), 319-327. DOI: 10.1016/S0021-9673(01)00572-6

Rottmann, L., and Heumann, K. G. (1994). "Development of an on-line isotope dilution technique with HPLC/ICP-MS for the accurate determination of elemental species," *Fresen. J. Anal. Chem*. 350(4-5), 221-227. DOI: 10.1007/BF00322473

Rowell, R. M., Pettersen, R., and Tshabalala, M. A. (2013). *Handbook of Wood Chemistry and Wood Composites*, CRC Press, Boca Raton, FL.

Saeed, A., Akhter, M. W., and Iqbal, M. (2005). "Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent," *Sep. Purif. Technol*. 45(1), 25-31. DOI: 10.1016/j.seppur.2005.02.004

Saeed, A., Iqbal, M., and Akhtar, M. W. (2002). "Application of biowaste materials for the sorption of heavy metals in contaminated aqueous medium," *Pak. J. Sci. Ind. Res*. 45(3), 206-211.

Saidur, A., Abdelaziz, E., Demirbaş, A., Hossain, M., and Mekhilef, S. (2010). "A review on biomass as a fuel for boilers," *Renew. Sust. Energ. Rev*. 15(5), 2262-2289. DOI: 10.1016/j.rser.2011.02.015

Sarin, V., and Pant, K. K. (2006). "Removal of chromium from industrial waste by using eucalyptus bark," *Bioresource Technol*. 97(1), 15-20. DOI: 10.1016/j.biortech.2005.02.010

Sarkanen, K. V., and Ludwig, C. H. (1971). *Lignins - Occurance, Formation, Structure and Reactions*, Wiley-Interscience, New York, USA.

Sarma, H. (2011). "Metal hyperaccumulation in plants: A review focusing on phytoremediation technology," *J. Environ. Sci. Technol*. 4(2), 118-138. DOI: 10.3923/jest.2011.118.138

Sarzanini, C., and Mentasti, E. (1997). "Determination and speciation of metals by liquid chromatography," *J. Chromatogr. A* 789(1-2), 301-321. DOI: 10.1016/S0021-9673(97)00988-6

Sepe, A., Ciaralli, L., Ciprotti, M., Giordano, R., Funari, E., and Costantini, S. (2003). "Determination of cadmium, chromium, lead and vanadium in six fish species from the Adriatic Sea," *Food Addit. Contam*. 20(6), 543-552. DOI: 10.1080/0265203031000069797

Sevilla, M., and Fuertes, A. B. (2009). "The production of carbon materials by hydrothermal carbonization of cellulose," *Carbon* 47(9), 2281-2289. DOI: 10.1016/j.carbon.2009.04.026

Sfakianakis, D. G., Leris, I., and Kentouri, M. (2011). "Effect of developmental temperature on swimming performance of zebrafish (*Danio rerio*) juveniles," *Environ. Biol. Fish*. 90(4), 421-427. DOI: 10.1007/s10641-010-9751-5

Sfakianakis, D. G., Renieri, E., Kentouri, M., and Tsatsakis, A. M. (2015). "Effect of heavy metals on fish larvae deformities: A review," *Environ. Res*. 137, 246-255. DOI: 10.1016/j.envres.2014.12.014

Sharma, V. K., Canditelli, M., Fortuna, F., and Cornacchia, G. (1997). "Processing of urban and agro-industrial residues by aerobic composting: Review," *Energ. Convers. Manage*. 38(5), 453-478. DOI: 10.1016/S0196-8904(96)00068-4

Sheng, P. X., Ting, Y. P., Chen, J. P., and Hong, L. (2004). "Sorption of lead, copper, cadmium, zinc and nickel by marine algal biomass: Characterization of biosorptive

capacity and investigation of mechanisms," *J. Colloid Interf. Sci.* 275(1), 131-141. DOI: 10.1016/j.jcis.2004.01.036

Shi, G., and Cai, Q. (2009). "Cadmium tolerance and accumulation in eight potential energy crops," *Biotechnol. Adv*. 27(5), 555-561. DOI: 10.1016/j.biotechadv.2009.04.006

Šoštarić, T. D., Petrović, M. S., Pastor, F. T., Lončarević, D. R., Petrović, J. T., Milojković, J. V., and Stojanović, M. D. (2018). "Study of heavy metals biosorption on native and alkali-treated apricot shells and its application in wastewater treatment," *J. Mol. Liq*. 259, 340-349. DOI: 10.1016/j.molliq.2018.03.055

Sjöström, E., and Alén, R. (1998). *Analytical Methods in Wood Chemistry, Pulping, and Papermaking*, Springer-Verlag, Berlin, Germany.

Søndergaard, J., Asmund, G., and Larsen, M. M. (2015). "Trace elements determination in seawater by ICP-MS with on-line pre-concentration on a Chelex-100 column using a 'standard' instrument setup," *MethodsX* 2, 323-330. DOI: 10.1016/j.mex.2015.06.003

Sperkova, J., and Suchanek, M. (2005). "Multivariate classification of wines from different Bohemian regions (Czech Republic)," *Food Chem*. 93(4), 659-663. DOI: 10.1016/j.foodchem.2004.10.044

Stumm, W. (1992). *Chemistry of the Solid-Water Interface: Process at the Mineral-Water and Particle-Water Interface in Natural Systems*, Wiley, New York, USA.

Su, P. (2012). *Sorption of Metal Ions to Wood, Pulp and Bark Materials*, Ph.D. Thesis, Åbo Akademi University, Turku, Finland.

Sud, D., Mahajan, G., and Kaur, M. P. (2008). "Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review," *Bioresource Technol*. 99(14), 6017-6027. DOI: 10.1016/j.biortech.2007.11.064

Sudha, B. R., and Abraham, E. (2003). "Studies on chromium (VI) adsorption using immobilized fungal biomass," *Bioresource Technol*. 87(1), 17-26. DOI: 10.1016/S0960-8524(02)00222-5

Suhas, P., Carrott, J. M., and Ribeiro Carrott, M. M. (2007). "Lignin - from natural adsorbent to activated carbon: A review," *Bioresource Technol*. 98(12), 2301-2312. DOI: 10.1016/j.biortech.2006.08.008

Suleiman, J. S., Hu, B., Huang, C., and Zhang, N. (2008). "Determination of Cd, Co, Ni and Pb in biological samples by microcolumn packed with black stone (Pierre noire) online coupled with ICP-OES," *J. Hazard. Mater*. 157(2-3), 410-417. DOI: 10.1016/j.jhazmat.2008.01.014

Sumida, T., Nakazato, T., Tao, H., Oshima, M., and Motomizu, S. (2006). "On-line preconcentration system using mini-column packed with a chelating resin for the characterization of seasonal variations of trace elements in seawater by ICP-MS and ICP-AES," *Anal. Sci*. 22(9), 1163-1168. DOI: 10.2116/analsci.22.1163

Sutton, K., Sutton, R. M. C., and Caruso, J. A. (1997). "Inductively coupled plasma mass spectrometric detection for chromatography and capillary electrophoresis," *J. Chromatogr. A* 789(1-2), 85-126. DOI: 10.1016/S0021-9673(97)00970-9

Świetlik, R., Trojanowska, M., and Rabek, P. (2012). "Distribution patterns of Cd, Cu, Mn, Pb and Zn in wood fly ash emitted from domestic boilers," *Chem. Spec. Bioavailab.* 25(1), 63-70. DOI: 10.3184/095422912X13497968675047

Takuwa, D. T., Sawula, G., Wibetoe, G., and Lund, W. (1997). "Determination of cobalt, nickel and copper in flowers, leaves, stem and roots of plants using ultrasonic slurry

sampling electrothermal atomic absorption spectrometry," *J. Anal. Atom. Spectrom.* 12(8), 849-854. DOI: 10.1039/A701266G

Tan, W. T., Ooi, S. T., and Lee, C. K. (1993). "Removal of chromium(VI) from solution by coconut husk and palm pressed fibres," *Environ. Technol*. 14(3), 277-282. DOI: 10.1080/09593339309385290

Tanner, S. D., Baranov, V. I., and Bandura, D. R. (2002). "Reaction cells and collision cells for ICP-MS: A tutorial review," *Spectrochim. Acta B* 57(9), 1361-1452. DOI: 10.1016/S0584-8547(02)00069-1

Tatar, E., Mihucz, V. G., Virag, I., Rácz, L., and Záray, G. (2007). "Effect of four bentonite samples on the rare earth element concentrations of selected Hungarian wine samples," *Microchem. J*. 85(1), 132-135. DOI: 10.1016/j.microc.2006.05.009

Taty-Costodes, V. C., Favdvet, H., Porte, C., and Delacroix, A. (2003). "Removal of cadmium and lead ions from aqueous solutions, by adsorption onto saw dust of *Pinus sylvestris*," *J. Hazard. Mater*. *B* 105(1-3), 121-142. DOI: 10.1016/j.jhazmat.2003.07.009

Tokareva, E. N., Pranovich, A. V., Ek, P., and Holmbom, B. (2010). "Determination of anionic groups in wood by time-of-flight secondary ion mass spectrometry and laser ablation-inductively coupled plasma-mass spectrometry," *Holzforschung* 64(1), 35-43. DOI: 10.1515/hf.2010.002

Tong, X. J., Li, J. Y., Yuan, J. H., and Xu, R. K. (2011). "Adsorption of Cu(II) by biochars generated from three crop straws," *Chem. Eng. J*. 172(2-3), 828-834. DOI: 10.1016/j.cej.2011.06.069

Tsezos, M. (1999). "Biosorption of metals. The experience accumulated and the outlook for technology development," *Process Met.* 9, 171-173. DOI: 10.1016/S1572-4409(99)80105-9

Tsezos, M. (2001). "Biosorption of metals: The experience accumulated and the outlook for technology development," *Hydrometallurgy* 59(2-3), 241-243.

Tsezos, M., Hatzikioseyian, A., and Remoudaki, E. (2012). "Biofilm reactors in mining and metallurgical effluent treatment: Biosorption, bioprecipitation, bioreduction processes," ResearchGate, (https://www.researchgate.net/publication/242547154_BIOFILM_REACTORS_IN_MINING_AND_METALLURGICAL_EFFLUENT_TREATMENT_BIOSORPTION_BIOPRECIPITATION_BIOREDUCTION_PROCESSES), Accessed 19 Dec 2018.

Tsezos, M., and Noh, S. H. (1987). "Particle encapsulation technique," U.S. Patent No. 4828882.

Turn, S. Q., Kinoshita, C. M., and Ishimura, D. M. (1997). "Removal of inorganic constituents of biomass feedstocks by mechanical dewatering and leaching," *Biomass Bioenerg.* 12(4), 241-252. DOI: 10.1016/S0961-9534(97)00005-6

Tuzen, M., and Soylak, M. (2007). "Multiwalled carbon nanotubes for speciation of chromium in environmental samples," *J. Hazard. Mater*. 147(1-2), 219-225. DOI: 10.1016/j.jhazmat.2006.12.069

Uchimiya, M., Chang, S., and Klasson, K. T. (2011). "Screening biochars for heavy metal retention in soil: Role of oxygen functional groups," *J. Hazard. Mater*. 190(1-3), 432-441. DOI: 10.1016/j.jhazmat.2011.03.063

Uchimiya, M., Lima, I. M., Klasson, K. T., Chang, S. C., Wartelle, L. H., and Rodgers, J. E. (2010). "Immobilization of heavy metal ions (Cu-II, Cd-II, Ni-II, and Pb-II) by

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broiler litter-derived biochars in water and soil," *J. Agr. Food Chem*. 58(9), 5538-5544. DOI: 10.1021/jf9044217

Ucun, H., Bayhan, Y. K., Kaya, Y., Cakici, A., and Algur, O. F. (2002). "Biosorption of chromium(VI) from aqueous solution by cone biomass of *Pinus sylvestris*," *Bioresource Technol*. 85(2), 155-158. DOI: 10.1016/S0960-8524(02)00086-X

Vanini, G., Souza, M. O., Carneiro, M. T. W. D., Filgueiras, P. R., Bruns, R. E., and Romao, W. (2015). "Multivariate optimisation of ICP OES instrumental parameters for Pb/Ba/Sb measurement in gunshot residues," *Microchem. J*. 120, 58-63. DOI: 10.1016/j.microc.2015.01.003

Vàzque, G., Antorrena, G., Gonzàlez, J., and Doval, M. D. (1994). "Adsorption of heavy metal ions by chemically modified *Pinus pinaster* bark," *Bioresource Technol*. 48(3), 251-255. DOI: 10.1016/0960-8524(94)90154-6

Veguería, S. F. J., Godoy, J. M., De Campos, R. C., and Gonçalves, R. A. (2013). "Trace element determination in seawater by ICP-MS using online, offline and bath procedures of preconcentration and matrix elimination," *Microchem. J*. 106, 121-128. DOI: 10.1016/j.microc.2012.05.032

Venkateswarlu, P., Ratnam, M. V., Rao, D. S., and Rao, M. V. (2007). "Removal of chromium from aqueous solution using *Azadirachta indica* (neem) leaf powder as an adsorbent," *Int. J. Phys. Sci*. 2(8), 188-195. DOI: 10.5897/IJPS

Viczián, M., Lásztity, A., Wang, X., and Barnes, R. M. (1990). "On-line isotope dilution and sample dilution by flow injection and inductively coupled plasma mass spectrometry," *J. Anal. Atom. Spectrom*. 5, 125-133. DOI: 10.1039/JA9900500125

Vieira, R. H. S. F., and Volesky, B. (2000). "Biosorption: A solution to pollution?," *Int. Microbiol*. 3(1), 17-24.

Vijayaraghavan, K., and Yun, Y.-S. (2008). "Bacterial biosorbents and biosorption," *Biotechnol. Adv*. 26(3), 266-291. DOI: 10.1016/j.biotechadv.2008.02.002

Vilardi, G., Ochando-Pulido, J. M., Verdone, N., Stoller, M., and Di Palma, L. (2018). "On the removal of hexavalent chromium by olive stones coated by iron-based nanoparticles: Equilibrium study and chromium recovery," *J. Clean. Prod*. 190, 200-210. DOI: 10.1016/j.jclepro.2018.04.151

Volesky, B. (1990). *Biosorption of Heavy Metals*, CRC press, Boca Raton, FL, USA.

Volesky, B. (1994). "Advances in biosorption of metals: Selection of biomass types," *FEMS Microbiol. Rev*. 14(4), 291-302. DOI: 10.1111/j.1574-6976.1994.tb00102.x

Volesky, B. (2003). *Sorption and Biosorption*, BV-Sorbex, Inc., Quebec, Canada.

Volesky, B. (2007). "Biosorption and me," *Water Res*. 41(18), 4017-4029. DOI: 10.1016/j.watres.2007.05.062

Volesky, B., and Holan, Z. R. (1995). "Biosorption of heavy metals," *Biotechnol. Progr*. 11(3), 235-250. DOI: 10.1021/bp00033a001

Volesky, B., and Tsezos, M. (1982). "Separation of uranium by biosorption," U.S. Patent No. 04320093.

Wan Ngah, W. S., and Hanafiah, M. A. K. M. (2008). "Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review," *Bioresource Technol*. 99(10), 3935-3948. DOI: 10.1016/j.biortech.2007.06.011

Wang, H. A., Grolimund, D., Giesen, C., Borca, C. N., Shaw-Stewart, J. R., Bodenmiller, B., and Günther, D. (2013). "Fast chemical imaging at high spatial resolution by laser ablation inductively coupled plasma mass spectrometry," *Anal. Chem*. 85(21), 10107-10116. DOI: 10.1021/ac400996x

Wang, L., and Dibdiakova, J. (2014). "Characterization of ashes from different wood parts of Norway spruce tree," *Chem. Eng. Transact*. 37, 37-42. DOI: 10.3303/CET1437007

Wang, K., Zhang, J., Shanks, B. H., and Brown, R. C. (2015a). "The deleterious effect of inorganic salts on hydrocarbon yields from catalytic pyrolysis of lignocellulosic biomass and its mitigation," *Appl. Energ*. 148, 115-120. DOI: 10.1016/j.apenergy.2015.03.034

Wang, L., Li, T., Güell, B. M., Løvås, T., and Sandquist, J. (2015b). "An SEM-EDX study of forest residue chars produced at high temperatures and high heating rate," *Energy Proced*. 75, 226-231. DOI: 10.1016/j.egypro.2015.07.312

Wase, D. A. J., Forster, C. F., and Ho, Y. S. (1997). "Low-cost biosorbents: Batch processes," in: *Biosorbents for Metal Ions*, J. Wase and C. Forster (eds.), CRC Press, London, England.

Wase, J., and Foster, C. (1997). *Biosorbent for Metal Ions*, Taylor and Francis, Ltd., London, England.

Wei, X., Brockhoff-Schwegel, C. A., and Creed, J. T. (2001). "A comparison of urinary arsenic speciation *via* direct nebulization and on-line photo-oxidation–hydride generation with IC separation and ICP-MS detection," *J. Anal. Atom. Spectrom*. 16(1), 12-19. DOI: 10.1039/B004257I

Werkelin, J., Skrifvars, B.-J., Zevenhoven, M., Holmbom, B., and Hupa, M. (2010). "Chemical forms of ash-forming elements in woody biomass fuels," *Fuel* 89(2), 481-493. DOI: 10.1115/FBC2005-78128

Wieser, M. E., and Schwieters, J. B. (2005). "The development of multiple collector mass spectrometry for isotope ratio measurements," *Int. J. Mass Spectrom*. 242(2-3), 97-115. DOI: 10.1016/j.ijms.2004.11.029

Wilson, G. W. T., Rice, C. W., Rillig, M. C., Springer, A., and Hartnett, D. C. (2009). "Soil aggregation and carbon sequestration are tightly correlated with the abundance of arbuscular mycorrhizal fungi: Results from long-term field experiments," *Ecol. Lett*. 12(5), 452-461. DOI: 10.1111/j.1461-0248.2009.01303.x

Wintz, H., Fox, T., and Vulpe, C. (2002). "Responses of plants to iron, zinc and copper deficiencies," *Biochem. Soc. T*. 30(4), 766-768. DOI: 10.1042/BST0300766

World Health Organization (WHO) (1992). "Cadmium," in: *Environmental Health Criteria*, WHO, Geneva, Switzerland.

Wu, F., Yang, W., Zhang, J., and Zhou, L. (2010). "Cadmium accumulation and growth responses of a poplar (*Populus deltoids×Populus nigra*) in cadmium contaminated purple soil and alluvial soil," *J. Hazard. Mater*. 177(1-3), 268-273. DOI: 10.1016/j.jhazmat.2009.12.028

Wu, J., and Boyle, E. A. (1997). "Low blank preconcentration technique for the determination of lead, copper, and cadmium in small-volume seawater samples by isotope dilution ICPMS," *Anal. Chem*. 69(13), 2464-2470. DOI: 10.1021/ac961204u

Xian, X., and Shokohifard, G. I. (1989). "Effect of pH on chemical forms and plant availability of cadmium, zinc and lead on polluted soils," *Water Air Soil Poll*. 45(3-4), 265-273.

bioresources.com

Yao, Y., Gao, B., Inyang, M., Zimmerman, A. R., Cao, X., Pullammanappallil, P., and Yang, L. (2011a). "Biochar derived from anaerobically digested sugar beet tailings: Characterization and phosphate removal potential," *Bioresource Technol*. 102(10), 6273-6278. DOI: 10.1016/j.biortech.2011.03.006

Yao, Y., Gao, B., Inyang, M., Zimmerman, A. R., Cao, X., Pullammanappallil, P., and Yang, L. (2011b). "Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings," *J. Hazard. Mater*. 190(1-3), 501-507. DOI: 10.1016/j.jhazmat.2011.03.083

Yoshida, S., Watanabe, M., and Suzuki, A. (2011). "Distribution of radiocesium and stable elements within a pine tree," *Radiat. Prot. Dosim.* 146(1-3), 326-329. DOI: 10.1093/rpd/ncr181

Yost, R. A., and Enke, C. G. (1978). "Selected ion fragmentation with a tandem quadrupole mass spectrometer," *J. Am. Chem. Soc*. 100(7), 2274-2275. DOI: 10.1021/ja00475a072

Zacchini, M., Pietrini, F., Mugnozza, G. S., Iori, V., Pietrosanti, L., and Massacci, A. (2009). "Metal tolerance, accumulation and translocation in poplar and willow clones treated with cadmium in hydroponics," *Water Air Soil Poll*. 197(1-4), 23-34. DOI: 10.1007/s11270-008-9788-7

Zeisler, R., Murphy, K. E., Becker, D. A., Davis, W. C., Kelly, W. R., Long, S. E., and Sieber, J. R. (2006). "Standard reference materials (SRMs) for measurement of inorganic environmental contaminants," *Anal. Bioanal. Chem*. 386(4), 1137-1151. DOI: 10.1007/s00216-006-0785-7

Zennaro, M., Cristofori, F., Formigoni, D., Frignani, F., and Pavoni, B. (2005). "Heavy metal contamination in compost. A possible solution," *Ann. Chim-Rome* 95(3-4), 247-256. DOI: 10.1002/adic.200590027

Zhang, N., Hu, B., and Huang, C. Z. (2007). "A new ion-imprinted silica gel sorbent for on-line selective solid-phase extraction of dysprosium(III) with detection by inductively coupled plasma-atomic emission spectrometry," *Anal. Chim. Acta* 597(1), 12-18. DOI: 10.1016/j.aca.2007.06.045

Zhang, N., Suleiman, J. S., He, M., and Hu, B. (2008). "Chromium (III)-imprinted silica gel for speciation analysis of chromium in environmental water samples with ICP-MS detection," *Talanta* 75(2), 536-543. DOI: 10.1016/j.talanta.2007.11.059

Zheng, G. D., Chen, T. B., Gao, D., and Luo, W. (2004). "Dynamic of lead speciation in sewage sludge composting," *Water Sci. Technol*. 50(9), 75-82. DOI: 10.2166/wst.2004.0539

Zheng, J., Hintelmann, H., Dimock, B., and Dzurko, M. S. (2003). "Speciation of arsenic in water, sediment, and plants of the Moira watershed, Canada, using HPLC coupled to high resolution ICP–MS," *Anal. Bioanal. Chem*. 377(1), 14-24. DOI: 10.1007/s00216-003-1920-3

Zhou, J. L., and Kiff, R. J. (1991). "The uptake of copper from aqueous solution by immobilized fungal biomass," *J. Chem. Technol*. 52(3), 317-330. DOI: 10.1002/jctb.280520305

Zhu, Y. G., Zhao, Z. Q., Li, H. Y., Smith, S. E., and Smith, F. A. (2003). "Effect of zinc–cadmium interactions on the uptake of zinc and cadmium by winter wheat (*Triticum aestivum*) grown in pot culture," *B. Environ. Contam. Tox*. 71(6), 1289-1296. DOI: 10.1007/s00128-003-0230-y

bioresources.com

Zouboulis, A. I., Lazaridis, N. K., and Matis, K. A. (2002). "Removal of toxic metal ions from aqueous systems by biosorptive flotation," *J. Chem. Technol. Biot*. 77(8), 958-964. DOI: 10.1002/jctb.663

Zougagh, A., Torres, A. G., Alonso, E. V., and Pavon, J. M. C. (2004). "Automatic on line preconcentration and determination of lead in water by ICP-AES using a TS-microcolumn," *Talanta* 62(3), 503-510. DOI: 10.1016/j.talanta.2003.08.033