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The Chemistry Behind the Use of Agricultural Biomass as Sorbent for Toxic Metal Ions: pH Influence, Binding Groups, and Complexation Equilibria

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1. Introduction

Waters, because of human activities, are often characterized by different kinds of contamination. In this chapter we will deal with contamination due to toxic metal ions. To purify wastewaters from these pollutants different treatment processes are applied, which include chemical precipitation, chemical oxidation or reduction, electrochemical treatment, membrane filtration, ion exchange, carbon sorption, and coprecipitation/sorption. A number of these processes are extremely expensive and some of them are ineffective at low concentrations. Alternative cost effective technologies based on low cost sorbents are nowadays of great concern in the applied research. These low cost sorbents must be abundant in nature, easily available, and above all they have to fit the worldwide request of recycling. Certain waste products from agricultural operations may become inexpensive sorbents and the potential of some of these wastes for the removal of a number of metal ions has been extensively investigated.

The use of these wastes as sorbents fulfills two important scopes for the protection of environment: the reuse of waste materials and the detoxification of wastewaters.

The biomass source depends on the agricultural production prevailing in the geographical areas where pollution and subsequent decontamination process take place.

The real challenge in the field of biosorption is to identify the chemical mechanism that governs metal uptake by biosorbents. Vegetal biomaterials, constituted principally by lignin, cellulose and by a non-negligible portion of fatty acid as major constituents, can be regarded as natural ion-exchange materials. Furthermore, the functional groups on the biomaterial surface, such as hydroxyl, carbonyl, amino, sulphydryl and carboxylic groups, allow the sorption of metal ions by strong coordination. Therefore, identification of the functional groups can help in shedding light on the mechanism responsible for metal uptake. Also some factors affecting the sorption process such as particle size, pH, metal ion concentration, agitation time, and kinetics must be investigated. The results obtained contribute to the knowledge of the overall process that takes place.

No doubt that metal removal from waste water by biomass requires a multidisciplinary approach (as do environmental sciences in general). The efforts of analytical chemists and solution equilibrium experts can give an important contribution to the knowledge and optimization of these processes.

The study of the chemical characteristics (complex formation constants, hydrolysis,…) of binding groups present on the biomass is of paramount importance to identify the mechanisms of metal sequestration, and to predict the selectivity towards the different cations, the strength of binding and the influence of pH on the sorption processes.

2. An overview of environmental pollution

Many elements play a double role in the physiology of living organisms; some are indispensable, while most of them are toxic at elevated concentrations. The concern on the potential toxic effects of metal ions has been increasing in recent years. As a result of industrial activities and technological development, heavy metals released into the environment pose a significant threat to environment and public health because of their toxicity, accumulation in the food chain and persistence in nature.

In the sixties of last century the importance of controlling the concentration of toxic metal ions in waters for human use became apparent after the Four Big Pollution Diseases of Japan, a group of manmade diseases all caused by environmental pollution due to improper handling of industrial wastes by Japanese corporations.

Two of the Four Big Pollution Diseases of Japan, Minamata (1932-1968) and Niigata disease (1965), were due to mercury poisoning. The first one, first discovered in Minamata in 1956, is a neurological disease characterized by ataxia, numbness in the hands and feet, general muscle weakness, narrowing of the field of vision and damage to hearing and speech, and in extreme cases, insanity, paralysis, coma and death. This poisoning was caused by the release of methyl mercury in the industrial wastewater from the Chisso Corporation's chemical factory. The highly toxic mercury has been bio-accumulated in shellfish and fish in Minamata Bay and the Shiranui Sea, and human and animals deaths continued over more than 30 years. In March 2001, 2265 victims had been officially recognized (1784 of whom had died) and, in addition, individual payments of medical expenses and a medical allowance had been provided to 10072 people in Kumamoto, Kagoshima and Niigata for their mercury related diseases (http://www.nimd.go.jp/english/index.html).

2.1 Main anthropogenic sources of toxic element pollution and their health effects

Environmental pollution, strictly interconnected to industrial spread, started in the most advanced countries. It is now diffused all over the world with a significant predominance in the emerging industrialized states. Varying factors contribute to the location of a large number of "potential polluting" industries in these countries due to the quite recent industrialization: source of raw materials (mines, forests, …), water availability, ready availability of manpower and its lower incidence on cost, laws not yet as restrictive as in advanced industrial countries. Actually, most raw matter is treated locally, not only for their natural resources, but also because of the lower cost of preliminary treatments. These treatments are the most hazardous, the heaviest and above all the most polluting.

In order to have a clear picture of the main anthropogenic sources of metal, or better said toxic element in general, pollution and their health effects, the sources, uses, correlated health disorders, and suggested concentration limits are reported in the following sections for each main polluting toxic element.

2.1.1 Aluminium

The element aluminium (atomic weight 26.98) is a silver white metal (density 2.7 g/mL). In its inorganic compound it presents only two oxidation states: 0, +3. Aluminium is the most abundant metal in the Earth's crust, and the third most abundant element, after oxygen and silicon. Because of its extremely low redox-potential potential in nature, it is found combined in over 270 different minerals as oxides or silicates. Aluminium is remarkable for low density and for its ability to resist corrosion due to the phenomenon of passivation.

Structural components made from aluminium and its alloys are vital to the aerospace industry and are very important in transportation and building. Aluminium compounds are widely used in the paper industry, in the dye production, in the textile industry, in processed food, and as a component of many cosmetic and pharmaceutical preparations.

Soluble aluminium salts have demonstrated toxic effects in elevated concentrations. Its toxicity can be traced to deposition in bone and the central nervous system. Because aluminium competes with calcium for absorption, increased amounts of dietary aluminium may contribute to osteopenia (reduced skeletal mineralization). In very high doses, aluminium can cause neurotoxicity. In a smaller amount it can give in susceptible people contact dermatitis, digestive disorders, vomiting or other symptoms upon contact or ingestion.

Owing to limitations in the animal data as a model for humans and the uncertainty surrounding the human data, a health-based WHO guideline value cannot be derived; however, practicable levels based on optimization of the coagulation process in drinking-water plants using aluminium-based coagulants are derived: 0.1 mg/L or less in large water treatment facilities, and 0.2 mg/L or less in small facilities (World Health Organization [WHO], 2008).

2.1.2 Arsenic

The element arsenic exists in three allotropes: grey arsenic, density 5.73 g/mL; yellow arsenic, density 1.93 g/mL; and non stable black amorphous arsenic, density 4.73 g/mL. Arsenic (atomic weight 74.92) shows metallic as well as non metallic properties. In its inorganic compound it presents different oxidation states: -3, 0, +3, +5. It is released into the air by volcanoes and is a natural contaminant of some deep-water wells. Arsenic is used to preserve wood, as a pesticide, to produce glass, in copper and other metal manufacturing, in the electronics industry and in medicine.

Occupational exposure to arsenic is common in the smelting industry (in which arsenic is a by-product) and in the microelectronics industry. Low-level arsenic exposure takes place in the general population through the use of inorganic arsenic compounds in common products such as wood preservatives, pesticides, herbicides, fungicides, and paints; through the consumption of foods treated with arsenic-containing pesticides; and through the burning of fossil fuels in which arsenic is a contaminant. The toxicity depends on its valence oxidation state and on its form inorganic or organic. In general, inorganic arsenic is more toxic than organic arsenic, and trivalent arsenite is more toxic than pentavalent and zero-valent arsenic. Arsenic, particularly in its trivalent form, inhibits critical sulphydryl-containing enzymes. In the pentavalent form, the competitive substitution of arsenic for phosphate can lead to rapid hydrolysis of the high-energy bonds in compounds such as ATP. The normal intake of arsenic by adults primarily occurs through ingestion and averages around 50 µg/d. After absorption, inorganic arsenic accumulates in the liver,

spleen, kidneys, lungs, and gastrointestinal tract. It is then rapidly cleared from these sites but leaves a residue in keratin-rich tissues such as skin, hair, and nails.

Guide line value for drinking water is 0.01 mg/L. It is a provisional value, as there is evidence of a hazard, but the available information on heath effects is limited (WHO, 2008).

2.1.3 Cadmium

Cadmium (atomic weight 112.41) is a silver white metal (density 8.65 g/mL). The oxidation states are 0, +2. The main uses of cadmium were steel production, non-ferrous metal production, refining, cement manufacture, cadmium plating, battery manufacture, waste and combustion, and phosphate fertilizers. Nowadays, because of concerns about its environmental toxicity, the use of cadmium has drastically decreased. About two thirds of the cadmium in use today come from nickel-cadmium batteries, the rest from pigments, metal plating and the plastic industry. It is a lot like lead and mercury, in that it accumulates both in the environment and in the body, causing long-term damage to life.

Cadmuim toxicity can manifest in a variety of syndromes, as hypertension, renal dysfunction, bone defects, hepatic injuries, lung damage, and reproductive effects. The maximum acceptable cadmium in drinking water is 0.003 mg/L (WHO, 2008).

2.1.4 Chromium

Chromium (atomic weight 51.99) is a lustrous, brittle, hard silver-gray metal (density 7.14 g/mL). It exists in different oxidation states: -2, 0, +2, +3, +6. Chromium is mainly used in steel production and in chrome plating. Its products are also used in leather tanning, printing, dye production, pigments, wood preservatives, and many others.

The respiratory and dermal toxicity of chromium are well-documented. Workers exposed to chromium have developed nasal irritation (at <0.01 mg/m^3, acute exposure), nasal ulcers, perforation of the nasal septum (at ~2 μg/m^3, subchronic or chronic exposure) and hypersensitivity reactions and "chrome holes" of the skin. Among the general population, contact dermatitis has been associated with the use of bleaches and detergents. Compounds of both Cr(VI) and Cr(III) have induced developmental effects in experimental animals that include neural tube defects, malformations, and fetal deaths. The speciation of chromium has become of relevant interest because of the association Cr(VI)-cancer. The different toxicity of the two forms Cr(VI) and Cr(III) are now under examination, even if at the moment the WHO Guidelines report the provisional value 0.05 mg/L referred to total chromium (WHO, 2008).

2.1.5 Copper

Copper (atomic weight 63.54) is ductile, lustrous, reddish metal (density 8.92 g/mL). The main application of copper is in electrical industry (transformers, generators, and transmission of electricity). Pollution derives from copper mining, brass manufacture, electroplating industries and from the use of its compounds in agriculture. Copper is known as one of the highest mammalian toxic compounds; inhalation of copper containing sprays is linked with an increase in lung cancer among exposed workers. Copper sulphate is widely used as an algaecide in water supply reservoirs affected by blooms of blue-green algae.

The maximum acceptable copper in drinking water is 2 mg/L (WHO, 2008).

2.1.6 Lead

Lead (atomic weight 207.19) is a bluish-grey, soft, dense metal (density 11.34 g/mL). The oxidation states are 0, +2, +4. Lead is extremely resistant to corrosion and is a poor conductor of electricity. Large quantities of lead, both as the metal and as the dioxide, are used in storage batteries. Lead is also used in cable covering, as ammunition, as electrodes, in solder and as roofing material. The metal is used as shielding from radiation, e.g. in x-ray rooms and nuclear reactors. Lead oxide is also used in the manufacture of fine crystal glass. Historically, lead was used in plumbing. Tetraethyl lead was used as an anti-knock agent in petrol, and as an additive in paints. These uses have been reduced recently because of environmental concerns about cumulative lead poisoning. Although lead is one of the most useful of all the metals, used since antiquity because of its wide distribution and its easiness to be extracted and to work with, it is also the metal that has the most damaging effects on human health.

Environmental contamination by lead probably dates back to Bronze Age. It can enter the human body through the uptake of food (65%), water (20%) and air (15%). Human activities, such as fuel combustion, industrial processes and solid waste combustion contribute to the rise of lead concentrations in the environment. Lead interferes with a variety of body processes and is toxic to many organs and tissues including heart, bones, intestines, kidneys, and reproductive and nervous systems. It interferes with the development of the nervous system and is therefore particularly toxic to children, causing potentially permanent learning and behavior disorders. Occupational exposure is a common cause of lead poisoning in adults. Lead can reach water through the corrosion of pipelines in water transportation systems. WHO Guidelines limit for lead in drinking water is 0.01 mg/L (WHO, 2008).

2.1.7 Mercury

Mercury (atomic weight 200.59) is a heavy, liquid at room temperature, silvery colored metal (density 13.53 g/mL). It presents the three oxidation states 0, +1, +2. The most modern uses are in batteries and cells. The Castner-Kellner process, that produces chlorine and sodium hydroxide, requires mercury in the entire process. It is furthermore used in thermometers, thermostats, switches, vacuum pumps, fluorescent and energy-saving lights, tooth fillings and electrical components. Many compounds of mercury have been used as medicines since many ages. However, in recent years, as awareness about the toxicity of mercury has increased amongst people, most of the medicines have become obsolete. Mercurochrome (used in cuts and wounds) and Thimerosal (as an dental amalgamation) are the compounds that are no more used in many countries. Mascara, an ingredient of cosmetics, contains some amounts of Thimerosal. During the past ten years mercury consumption has shown a strong upward trend. The major proportion can be accounted for by the chloro-alkali industry, from which mercury is released into the environment. Most of it finds its way to watercourses exposing aquatic ecosystems where mercury accumulates. The use of seed-dressings containing mercury is decreasing, although this use of mercurial's is still considerable, and in view of findings in other countries elevated mercury levels in seed-eating birds and their predators must be expected. Many states in the US are now very strict against the use of mercury in cosmetics and medicines. Mercury in the form of gaseous vapors is used in mercury vapor lamps, neon signs and fluorescent lamps.

Biological properties of mercury are very important and include these characteristics: inhaled mercury is more dangerous than ingested mercury; human workers and handlers of mercury may become contaminated and mercury-diseased; elemental and inorganic

mercury can be transformed to the extremely toxic methyl-mercury (CH_3Hg^+) by some microbes; mercury accumulates in living organisms, cells, tissues, organs and organisms; mercury can damage immune cells and tissues, and organs such as brain, heart, kidneys, lungs; mercury can be concentrated in the environment and then magnified upwards along the food chain (bioaccumulation and bio-magnification); all compounds of mercury, except those not soluble in water, are to be considered poisonous regardless of the manner of inhalation or ingestion. Mercury limit in drinking water is 0.006 mg/L (WHO, 2008).

2.1.8 Nickel

Nickel (atomic weight 58.69) is a ductile, malleable, silver-white metal (density 8.91 g/mL). It presents the oxidation states -1, 0, +1, +2, +3, +4. More than 70% of nickel produced annually is devoted to the production of alloys; nickel is used in a variety of electrolytic procedures, in the manufacture of batteries and in welding procedures, as a catalyst in large scale processes, and in the glass and ceramics industry. In addition to 8.5 million tons per year of nickel in the atmosphere due to natural sources, 43 million tons are released by anthropogenic activities. Population exposed at soluble nickel concentration < 1 μg m^{-3} has no respiratory cancer risk, which is related to exposure to concentrations greater than 1 mg m^{-3} (workers in nickel industries). Dermal sensitivity to nickel is presented by 10-20 % of female and 1 % of male population. The nickel content in surface water ranges from 2 to 20 μg/L. The limit for nickel in drinking water is 0.07 mg/L (WHO, 2008).

2.1.9 Zinc

Zinc (atomic weight 65.41) is a soft, bluish-white metal (density 7.14 g/mL). It presents the oxidation states 0, +2. Zinc and its products are widely used in alloy production, as anticorrosion coatings of steel and iron, in electrical devices, in rubber and tire industries, in paints, in pesticides and as chemical reagents in a number of applications. Zinc is the second most abundant trace metal in the human body: it appears in the active site of a variety of enzymes and many of the metabolic consequences of its deficiency are related to a diminished activity of zinc metallo-enzymes. Zinc is relatively nontoxic, even if daily doses greater than 100 mg during several months may lead to different disorders. Zinc imparts an undesirable astringent taste to water. Water containing zinc at concentrations in the range 3–5 mg/L also tends to appear opalescent and develops a greasy film when boiled. This feature allows the high zinc limit 3 mg/L in drinking water (WHO, 2008).

3. Interaction between biomass and metal ions

The capacity of a given biomass to absorb toxic metal ions has been traditionally quantified using either Langmuir, Freundlich, Langmuir–Freundlich isotherms, or different alternative models. These isotherms were developed under chemical assumptions that are not generally met in biosorption processes.
The main reason for their extended use is that they describe satisfactorily experimental data. They can be used for predictions, although they do not take into account external parameters, such as the pH or ionic strength. Langmuir equation

$$q_{eq} = q_{max}\, b\, C_{eq} / \, (1 + b\, C_{eq}) \tag{1}$$

is the simplest and the one used by the most of authors. In this equation, q_{eq} is the amount of metal ion sorbed at equilibrium, C_{eq} the equilibrium concentration of metal ion in solution and b is the Langmuir constant related to the energy of sorption, which reflects quantitavely the affinity between the biomass and the metal ion. The parameter q_{max} represents the maximum capacity of the biomass to absorb a given metal ion and it is usually determined by fitting the isotherm experimental data to the equation model. The q_{max} values are quite almost expressed as milligrams of sorbed metal ion respect to the weight in grams of dry sorbent.

The q_{max} values reported in an our recent paper (Nurchi & Villaescusa, 2008), based on the survey of last ten years of literature, lie in the ranges 2.81-285.7 mg/g for Cd^{2+}, 11.7-32.00 mg/g for Cu^{2+}, 8.45-73.76 mg/g for Pb^{2+}, 1.78-35 mg/g for Zn^{2+}, 7.9-19.56 mg/g for Ni^{2+}, 17.2-126.9 mg/g for Cr(VI), and 3.08 mg/g for Cr^{3+}. These quantities look more similar when expressed in molar concentrations (0.025-2.5 mmol/g for Cd^{2+}, 0.185-0.50 mmol/g for Cu^{2+}, 0.04-0.36 mmol/g for Pb^{2+}, 0.027-0.53 mmol/g for Zn^{2+}, 0.13-0.34 mmol/g for Ni^{2+}, 0.33-2.44 mmol/g for Cr(VI), and 0.06 mmol/g for Cr^{3+}) and the maximum quantity of metal ion sorbed by a gram of sorbent is of the order of 0.5 mmoles (values five times higher are found for Cd^{2+} and Cr(VI), which could be considered a reasonable result if we consider the large variability in materials and experimental conditions (particle size, pH, temperature, etc.).

In order to better characterize the behavior of a given sorbent, the use of chemical (mmol/g) instead of technical (mg/g) units has to be recommended whenever comparisons have to be made. The results obtained in this way actually contain information on the number of coordinating sites, which can be of great utility to make provisional forecasts of the binding capacity of different metal ions, without restraints due to their atomic mass.

In literature different variables (particle size, temperature, pH, exchange and so on), and different kinetics and thermodynamic models (Langmuir, Freundlich, ...) are taken into account. In the following sections 5 and 6 we will discuss the effect of temperature and pH on the sorption process. In order to design sorption processes, it is important to predict the rate at which a pollutant is removed from an aqueous solution. The rate constant and reaction order must be determined experimentally. It is usually necessary to carry out experimental studies varying several parameters such as metal ion and sorbent concentration, agitation speed, particle size, and temperature. Fitting the experimental results allows determining the kinetic mechanism, e.g. film diffusion, kinetic sorption, diffusion sorption or a combination of these processes. The kinetic models most used in biosorption studies were widely discussed in an intersting review by Ho et al., 2000.

4. Identification of functional groups and their role in metal sorption

The sorption of metal ions by biomass occurs via functional groups on its surface by one or more mechanisms. All the sorbents derived from different by-products of agriculture share a common network of lignin and cellulose, and differ for the presence of functional groups which characterize each single biomass. As said before, identification of the functional groups is crucial for understanding the mechanism that governs the sorption process. Indeed, each functional group presents its own coordinating abilities toward the different metal ions. These coordinating abilities can be rationalized in term of the hard/soft character both of the binding group and of the metal ion. In order to highlight the importance of each different binding group in the mechanism of metal ion adsorption, the percent incidence drawn out from 1997 to nowadays literature is presented in Fig. 1.
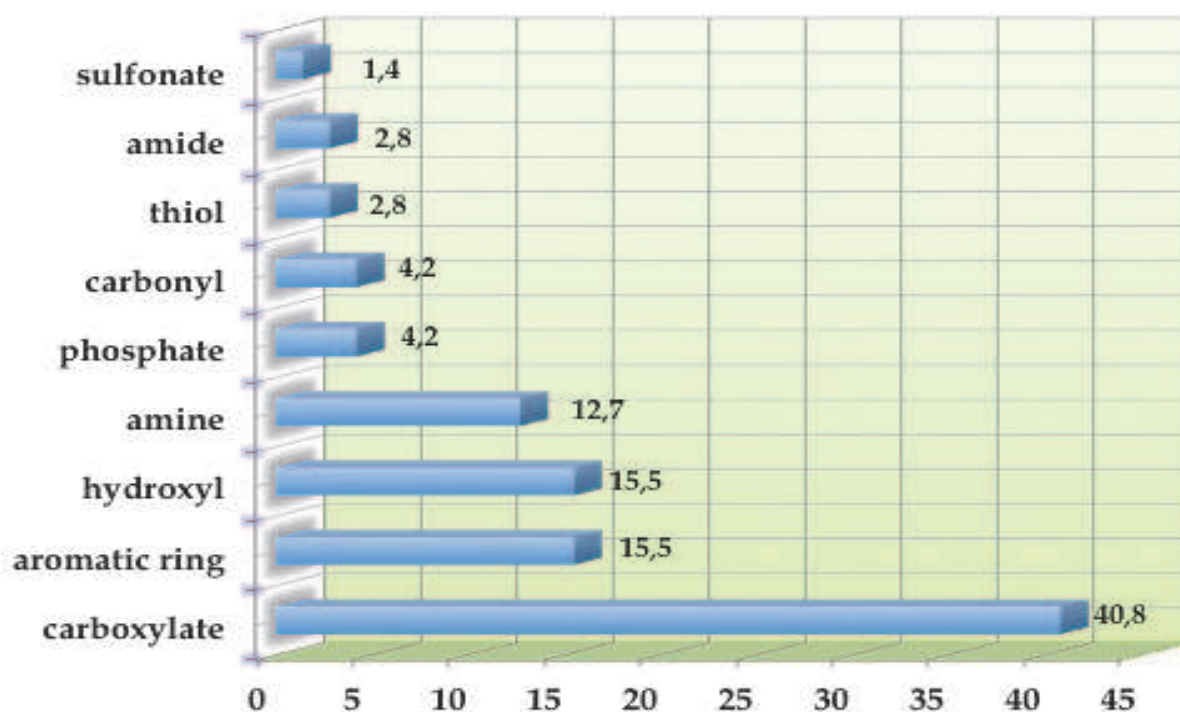
Fig. 1. Incidence of the different binding groups on biomass surface involved in metal ion complexation.

Potentiometric titrations, chemical treatments of the sorbent, alkaline and alkaline-earth metal ion release and spectroscopic techniques are the procedures widely followed to reveal the binding groups. A brief survey of these methods is presented in the next sections.

4.1 Potentiometric titrations

Potentiometric titrations measure the acid-base properties of the sorbent and the ionic exchange properties with regard to H^+ and OH^- ions. The presence of acid and basic sites determines the sorbent amphoteric properties and, depending on the pH, the functional groups can be either protonated or deprotonated. Active site concentrations are generally determined by acid-base potentiometric titration of the adsorbent and related modeling. Acidity constants found in the literature can be considered as mean values, which are representative of the class of the functional groups. Potentiometric titrations can also be used to determine the pH at the point zero charge (pH_{pzc}) of biomass. pH_{pzc} is the pH at which the sorbent surface charge takes a zero value as the charge of the positive surface sites is equal to that of the negative ones.

The knowledge of pH_{pzc} allows one to hypothesize on the ionization of functional groups and their interaction with metal species in solution; at solution pH's higher than pH_{pzc} the sorbent surface is negatively charged and could interact with metal positive species while at pHs lower than pH_{pzc} the solid surface is positively charged and could interact with negative species. Carboxylic groups were found to be the most involved, in the majority of cases, where potentiometric titration was used to elucidate the functional groups on biomass responsible for metal ions sorption. This fact is in part expected on the basis of their easiest deprotonation in the 2 - 6 pH range which is the most suitable for metal sorption.

4.2 Chemical treatment of sorbent surface

The contribution of each functional group can be evaluated by chemical treatment. It consists in carrying out chemical reactions that selectively block different functional groups on the sorbent surface. The most common chemical modifications are esterification of carboxylic and phosphate groups, methylation of amines, and modification of mercapto groups. Carboxylic groups can be alkylated by reaction with methanol or ethanol in acidic media, while amines by reaction with formaldehyde and formic acid. Alkylation of both functional groups prevents their participation in metal biosorption, thus reducing the biosorption efficiency.

Chemical treatments were also used to selectively extract different compounds, such as fats or polyphenols, in order to improve metal sorption. A report on the application of these methods can be found in a work of Nurchi at al., 2010.

4.3 Alkaline and alkaline-earth metal ion release

Vegetal biomaterial can be viewed as a natural ion-exchange material that primarily contains weak acidic and basic groups on its surface. One of the common procedures to investigate whether ion-exchange is the mechanism responsible for metal sorption is to determine the concentration of alkaline and alkaline-earth metal ions or protons (when the sorbent is pretreated with acid) released from the sorbent to the solution after metal uptake.

The determination of the concentration of ions released into the solution (M: Na^+, K^+, Ca^{2+}, Mg^{2+}, H^+) allows the balance of the concentration of the absorbed toxic metal ion (M*), through a charge balance, not explicitly reported in equation (2).

$$R-M + M^* \rightleftarrows R-M^* + M \qquad (2)$$

On the solid material the appearance of the sorbed metals, associated with the disappearance of alkaline and alkaline-earth metal ions, can be followed by Scanning Electron Microscopy (SEM) coupled with energy dispersive X-ray analysis (EDAX). This technique greatly contributes to indicate that ion exchange takes place between alkaline and alkaline-earth metal ions on the sorbent and the toxic metal ions in the solution.

4.4 Spectroscopic analysis

Useful information on the role of functional groups on metal sorption can be reached by non-destructive spectroscopic methods, observing the modifications induced by the metal on the spectra of the pure adsorbent.

4.4.1 Fourier transform infrared spectroscopy (FTIR)

FTIR is one of the most used techniques. Infrared Spectroscopy belongs to the group of molecular vibrational spectroscopies which are molecule-specific, and give direct information about the functional groups, their kind, interactions and orientations. Its sampling requirements allow the gain of information from solids, and in particular from solid surfaces. Even if historically IR has been mostly used for qualitative analysis, to obtain structural information, nowadays instrumental evolution makes non-destructive and quantitative analysis possible, with significant accuracy and precision. The shift of the bands and the changes in signal intensity allow the identification of the functional groups involved in metal sorption. Using this technique, carbonyl, carboxylic, aromatic, amine, and hydroxyl groups has been found to be involved in metal uptake by different biosorbents.

4.4.2 Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS)

DRIFTS occurs when light strikes on the surface of a material and is partially reflected and transmitted. The light that penetrates the material may be absorbed or reflected out again. The diffuse reflectance (radiation reflected from an absorbing material) is thus composed of surface-reflected and bulk re-emitted components, and contains information relative to the structure and composition of the sample. Even if DRIFTS has been not of large use, it has found interesting applications on verifying the enhancement of cadmium sorption capacity by juniper wood when carbonyl groups were substituted by sulfonic groups and on determining that Cr^{3+}, Cu^{2+} and Zn^{2+} were sorbed onto the organic polymeric fraction of olive mill wastewater by ion exchange between alkaline and alkaline-earth metal ions and protons bound to carboxylic groups.

4.4.3 X-ray absorption spectroscopy (XAS)

XAS specifically examines the local structure of elements in a sample. The structure of a material is deduced on theoretical basis, but usually the interpretation of XAS spectra is founded on databases of known structures. This technique is useful in the case of heterogeneous samples and a wide variety of solid materials can be examined directly and non-destructively. Also the structure of amorphous phases can be easily achieved, as the local structure does not depend on long-range crystalline order. The application of XAS varies from the trace element concentration up to that of major elements. So it is useful to speciate trace elements adsorbed on the surface of biomass. X-ray absorption spectroscopy consists in the absorption of high energy X-rays by an atom in a sample. This absorption takes place at the energy corresponding to the binding energy of the electron in the sample. The interaction of ejected electrons with the surrounding atoms produces the observed spectrum. (XAS) and extended X-ray absorption fine structure (EXAFS) were used to ascertain the ligands involved in metal binding and the coordination environment for Cr^{3+} bound to *alfalfa shoot* biomass by Tiemann et al., 1999, and by Gardea-Torresday et al., 2002.

4.4.4 X-ray photoelectron spectroscopy (XPS)

XPS, introduced by the Nobel Prize winner Siegbahn in 1949, is the main technique used for qualitative and quantitative elemental analysis of surfaces. It provides significant information on the chemical bonding of atoms. The absorption of high-energy electromagnetic radiation (X-ray or UV) by surfaces leads to the emission of photoelectrons; those generated in the outermost layers emerge from the surface into the vacuum and can be detected. The measure of the kinetic energy of the emitted photoelectrons allows the determination of the binding energies of electrons and the intensity function (number of photoelectrons vs. kinetic energy), and quantitative results are obtained from the knowledge of the number of atoms involved in the emission process.

Ashkenazy et al., 1997, using X-Ray photoelectron spectroscopy (XPS) pointed out the involvement of nitrogen in lead sorption and the lead-oxygen interaction at the carboxyl group on the basis of the decrease in nitrogen concentration and of the shift of oxygen peak. The same technique confirmed that chromium was sorbed onto grape stalks in both its trivalent and hexavalent forms, and allowed the ascertainment of the oxidation state of chromium bound on pine needles. Furthermore it was used to explain the increase of cadmium and lead sorption onto baker's yeast after modification of sorbent surface by cross linking cysteine.

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4.4.5 Scanning-electron microscopy (SEM)

SEM is a useful technique in the study of both the natural sorbent morphology and its modification derived from sorbate interactions. SEM is an electron microscope, which provides images of the sample surface by scanning it with a high-energy beam of electrons. The electron interactions with the atoms of the sample produce signals that contain information about topography, morphology, and composition of the sample surface. The samples must be electrically conductive, at least on their surface, for conventional SEM imaging. Nonconductive samples are coated with an ultra-thin layer of electrically-conducting material; this coating prevents the accumulation of static electric charges on the sample surface during electron irradiation. Magnification of the imaging can be controlled over a range of up to 6 orders of magnitude from about x25 to 250,000 times. When coupled with energy dispersive X-ray analysis (EDAX), the atom concentrations on the sorbent surface can be determined. This enables the confirmation of a mechanism of ion exchange, generally investigated by determining the concentration of alkaline and alkaline-earth metal ions released from the sorbent after metal sorption.

5. Effect of temperature

In studies on heterogeneous material, requiring long equilibration times, it is hard to perform reliable calorimetric measurements. Thus, only carrying out experiments at variable temperature can give information on how this parameter affects the sorption of metal ions. From the limited extent of studies at variable temperature, only controversial conclusions can be reached. Most studies have been carried out at a fixed room temperature (20 or 25 °C). Some studies point out a low temperature influence or, at least, in a limited temperature range, giving evidence that ion exchange is the mechanisms responsible for the sorption process. Nevertheless, Kapoor and Viraraghavan, 1997, remarked that biosorption reactions are normally exothermic, which indicates that sorbent capacity increases with decreasing temperature. Conversely, Romero-González et al., 2005, found that the sorption capacity of Agave lechuguilla leaves for Cr(VI) sorption increased on increasing the temperature from 10 to 40 °C, justifying this endothermicity with Cr(VI) reduction to Cr(III). Malkoc and Nuhoglu, 2007, confirmed the endothermicity of Cr(VI) sorption on tea factory waste, metal uptake increasing as temperature increas from 25 °C to 60 °C. The favorable temperature effect was attributed to a swelling effect within the internal structure of the sorbent enabling the large metal ions Cr(VI) to penetrate further.

6. Effect of pH on sorption

As we have already discussed in section 4.3, one of the mechanisms involved in the sorption of positively charged metal species is ion-exchange. Vegetal biomaterials (constituted principally by lignin and cellulose as major constituents and by a non negligible portion of fatty acid, bearing functional groups such as alcohol, ketone and carboxylic groups that can be involved in complexation reactions with metallic cations) can be viewed as natural ion-exchange materials. These materials primarily contain weak acid and basic groups on the surface, whose ionization degree strongly depends on the pH of the solution. Several authors have performed potentiometric titrations to investigate acid-base properties on the surface of biosorbents and to determine the number of active sites for metal ion sorption.

The strong pH dependence of the sorption parameters can depend on several factors, which can be simplified as follows:

1. behaviour and speciation of metal ions;
2. dependence of the acid-base characteristics of the adsorbing material on the pH;
3. dependence of the interaction metal ion-sorbent on the pH.

As far as point 1 is concerned, we report a statement made by Baes and Mesmer, 1976, in their classical book on the hydrolysis of cations: "*soluble hydrolysis products are important when cation concentrations are very low and can profoundly affect the chemical behaviour of the metals; the formulas and charges of the hydrolysis products formed in such systems can control such important aspects of chemical behaviour as:*

a. *sorption of the dissolved metals in mineral and soil particles;*
b. *tendency of metal species to coagulate colloidal particles;*
c. *solubility of the hydroxide (or oxide) of the metals;*
d. *extent to which the metals can be complexed in solution or extracted from solution by natural agents;*
e. *oxydizability or reducibility of the metals to another valence state.*"

Based on these considerations, we demonstrate the influence of pH on sorption taking as an example the behaviour of one of the most important toxic metal ion, lead, in presence of different coordinating groups. Firstly we take into account the hydrolysis of this metal ion at two different concentrations, 100 mg/L and 0.05 mg/L, i.e. at concentration in strong polluted water and at concentration equal to EU recommended value for drinking water (Fig. 2). At 100 mg L^{-1}, the species $Pb(OH)^+$ (pH> 6) and the polynuclear species $Pb_3(OH)_4^{2+}$ and $Pb_6(OH)_8^{4+}$ (pH >7) are formed before hydroxide precipitation occurs at pH~9.5; at 50 µg L^{-1}, Pb^{2+} do not form precipitates and only the mononuclear species are formed instead of the polynuclear ones observed at 100 mg L^{-1}. Metal ion hydrolysis equilibria, as well as hydroxide precipitation, can help explain the dependence of metal ion sorption on the pH. In most cases, the observed pH dependence lies in a range in which the metal ion is completely insensitive to the acidity of the medium. In metal ion sorption, pH effects are commonly accounted for by charge variations on the sorbent surface: protonation of basic sites or dissociation of acidic groups. According to the majority of authors a negative charge favours metal ion sorption by an ionic exchange mechanism or by electrostatic interactions, i.e. the sorption is completely determined by the acid-base behaviour of the functional groups on the surface of the adsorbing material.

The real behaviour is certainly far more complex and can be rationalised in terms of metal ion coordination by surface binding groups. The presence of phenolic, carboxylic, catecholic, amino, and mercapto groups on the surface is well known. As a working hypothesis we can imagine that the different binding groups on the solid particles, dispersed in the metal ion solution, behave as different ligands. With this simplifying assumption, we can consider our system as set of solution equilibria. In this assumption we can treat our system as solution equilibria between various ligands competing for a metal ion or for various metal ions. For example, a carboxylic group near a phenolic group on the surface can be assumed to behave as a salicylate ligand, limited to form only 1:1 chelates being anchored to a solid surface.

In the example showed in Fig. 3, we took into consideration three different coordinating groups as possible ligands for lead: COOH, hard, NH_2, intermediate, and SH, soft donors. Furthermore, we also considered all the possible combination of them to obtain bidentate ligands, COOH-COOH; COOH-NH_2, COOH-SH, NH_2-NH_2, NH_2-SH, and SH-SH.

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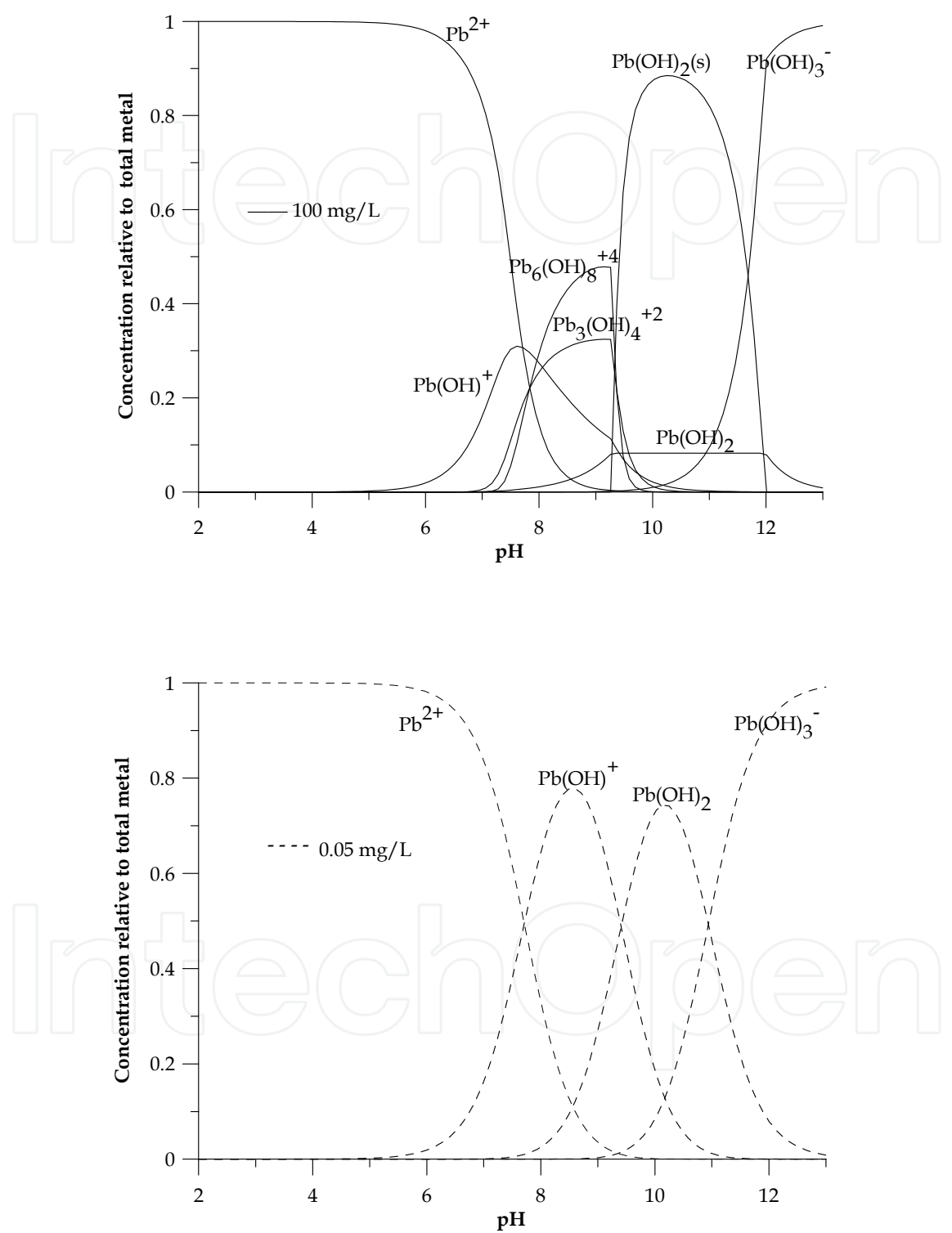
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Fig. 2. Species distribution diagrams for Pb^{2+} hydrolysis at two different total concentration 100 mg/L (solid lines) and 0.05 mg/L (dashed lines).
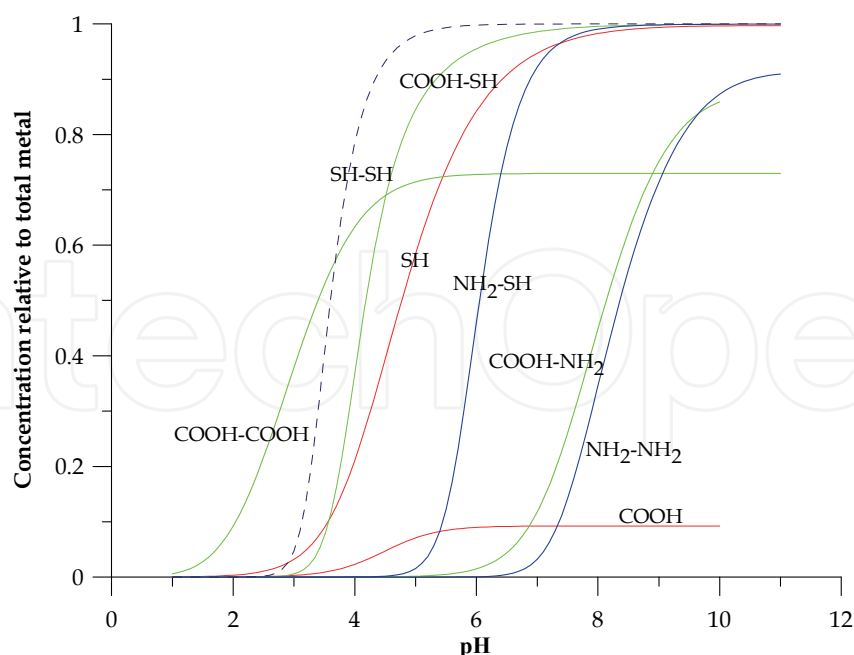
Fig. 3. Formation curves for complex formation between Pb^{2+} and various ligands, bearing the coordinating groups reported on the plots, calculated for 0.001 M solutions in both Pb^{2+} and ligand.

Starting from the distribution curves, obtained using the literature constants for lead complexes with different ligand bearing the above mentioned coordinating groups, some conclusions can be drawn. The soft metal Pb^{2+} ion prefers the soft SH group, which became completely coordinated in 4-6 pH range. No data is available in literature for a single NH$_2$-Pb interaction. The carboxylic group forms a weak complex in the pH range corresponding to its deprotonation. The addition of a second group (COOH or SH) to the starting SH favours lead coordination, while the addition of a NH$_2$ group has an adverse effect. Two vicinal COOH groups allow lead complexation at low pH values and act much better than a single COOH group, even if the per cent of complex formation is still much lower than that reached by SH groups. Regarding the coordinating properties related to the amino group, the complex formation, taking place at basic pH > 7, does not prevent the hydroxide formation.

7. Conclusion

The numerous studies on metal sorption by biomass are extremely spread: the investigation of the mechanism involved in metal ion sorption is performed by different techniques, methods and approaches that are related to the equipment availability in the researcher's laboratories and to the researcher education. The use of highly sophisticated and extremely expensive techniques, as mentioned in the above sections, enables one to obtain structural information on the sorbent morphology and indirect knowledge of the implied sorption mechanisms, by comparing some physical properties of the material before and after metal sorption. Even if little importance is given to the classical chemical methods, such as potentiometry and alkaline and alkaline-earth metal ion release, these on the contrary offer several advantages, such as the easy availability in all laboratories, the fact that they are fast,

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cheap, and friendly-used. The main benefit of these methods is the attainment of quantitative results, which allow the evaluation of the amount and the kind of functional groups involved and the amount of exchanged metal ions.

We hope that the achievements obtained from this enormous quantity of research works can lead in the coming years to a real outlet of practical applications, even if a lack of protocol or systematic approach in this kind of studies has to be remarked. Furthermore, the reached level of knowledge acquired should allow the classification of biomass on the basis of structural coordinating groups on its surface, essential to forecast their behavior toward the different toxic metal ions. Thank to this information, it will be possible to depict the strength of interaction and the pH range more useful for metal removal.

The application of biosorption for effluent detoxification will have a strong ecological impact, joining the advantage of recycling waste biomass and of purifying contaminated waters from toxic metal ions.

8. Acknowledgment

9. References

Ashkenazy, R., Gottlieb, L., & Yannai, S. (1997). Characterization of acetone-washed yeast biomass functional groups involved in lead biosorption. *Biotechnology and Bioengineering*, Vol. 55, No. 1, (July 1997), pp. 1–10, ISSN 0006-3592.

Baes, C. F.Jr. & Mesmer, R.E. (1976). *The hydrolysis of cations*, J. Wiley & Sons, Inc., ISBN 0-471-03985-3, New York.

Ho, J Y.S., Ng, C.Y., & Mckay, G. (2000). Kinetics of pollutant sorption by sorbents: Review. *Separation and Purification Reviews*, Vol. 29, pp. 189-232, ISSN 1542-2119.

Kapoor, A., & Viraraghavan, T. (1997). Fungi as biosorbents, In: *Biorsorbents for metal ions*, Wasedaj & Foster, pp. 67-80, Taylor & Francis, ISBN 074840431, London.

Malkoc, E., & Nuhuglu, Y. (2007). Potential of tea factory waste for chromium(VI) removal from aqueous solutions: Thermodynamic and kinetic studies. *Separation and Purification Technology*, Vol. 54, No. 3, (May 2007), pp. 291-298, ISSN 1383-5866.

Nurchi, V.M., &Villaescusa, I. (2008). Agricultural biomasses as sorbents of some trace metals. *Coordination Chemistry Reviews*, Vol. 252, (May 2008), pp. 1178-1188, ISSN 00108545.

Nurchi, V.M., Crisponi, G., & Villaescusa, I. (2010). Chemical equilibria in wastewaters during toxic metal ion removal by agricultural biomass. *Coordination Chemistry Reviews*, Vol. 254, (September 2010), pp. 2181-2192, ISSN 00108545.

Romero-Gonzales, J., Peralta-Videa, J. R., Rodriguez, E., Ramirez, S. L.,& Gardea-Torresdey, J. L. (2005). Determination of thermodynamic parameters of Cr(VI) adsorption from aqueous solution onto Agave lechuguilla biomass. *The Journal of Chemical Thermodynamics*, Vol. 37, No. 4, (April 2005), pp. 343-347, ISSN 0021-9614.

Tiemann, K.J., Gardea-Torresdey, J.L., Gamez, G., Dokken, K., Sias, S., Renner, M.W., & Furenlid, L.D. (1999). Use of X-ray Absorption Spectroscopy and Esterification to

Investigate Cr(III) and Ni(II) Ligands in Alfalfa Biomass. *Environmental Science & Technology*, Vol.33, (December 1998), pp. 150-154, ISSN 0013-936X.

World Health Organization (Ed.). (2008). *Guidelines for drinking-water quality,* World Health Organization, ISBN 9241546743, Geneva.
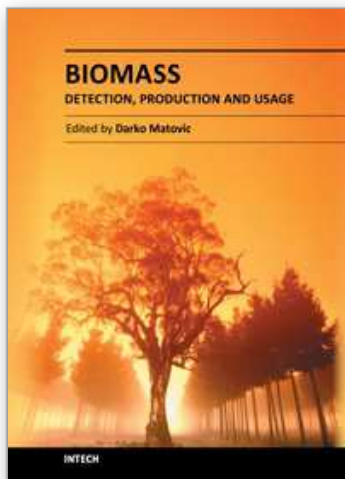
Biomass - Detection, Production and Usage

Edited by Dr. Darko Matovic

Biomass has been an intimate companion of humans from the dawn of civilization to the present. Its use as food, energy source, body cover and as construction material established the key areas of biomass usage that extend to this day. Given the complexities of biomass as a source of multiple end products, this volume sheds new light to the whole spectrum of biomass related topics by highlighting the new and reviewing the existing methods of its detection, production and usage. We hope that the readers will find valuable information and exciting new material in its chapters.

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