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Review

Agricultural biomasses as sorbents of some trace metals

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Contents

Abstract

The studies of sorption of six metal ions (Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cr^{3+} and Cr(VI)) from by-products of agriculture are taken into account. The Langmuir q_{max} values obtained with the use of different biomasses are evaluated and, in order to acquire comparable results, the necessity of using molar concentrations is stressed. The main effects of pH on sorption are estimated by considering both the behaviour of metal ions (hydrolysis and hydroxide precipitation) and the effect of pH on coordination, using a simulated example. Some considerations are made on the information that can be obtained using the most common isotherms and on the need to use chemical dimensions rather than weight in order to make comparison among various metal ions (since atomic weight differences deeply alter the significance of parameters in non-chemical units) and to predict the effects of competition between two (or more) of these for the same sorbent sites on the biomass surface.

Keywords: Agricultural biomasses; Metal ions; Sorption; Isotherms; pH effects

1. Introduction

Aqueous wastes from a number of industrial activities, such as metal plating facilities, mining operations, tanneries, metallurgical plants and the paint industry are often characterized by

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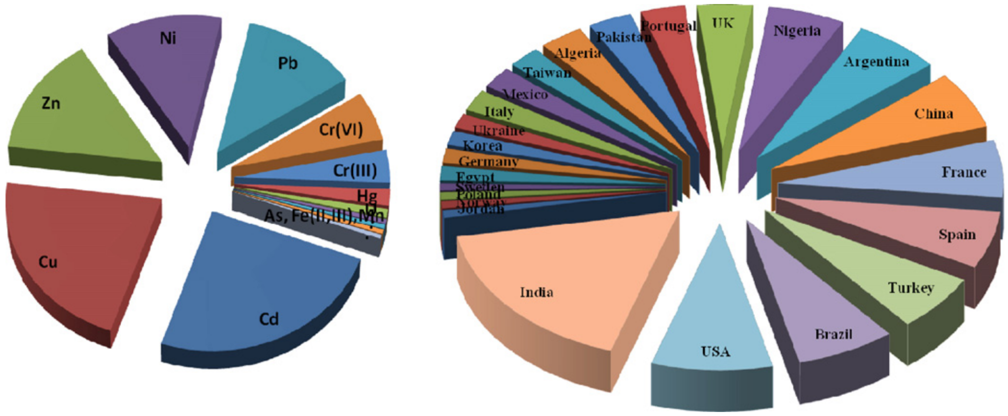

Fig. 1. (Left) Percentage interest in each metal ion in the literature on the use of agriculture biomasses for wastewater treatment. (Right) Countries involved in studies on the use of agriculture biomasses for wastewater treatment.

heavy metal[1] contamination. Heavy metals are not biodegradable and tend to accumulate in living organisms causing various diseases and disorders. As reported by Bailey et al. [1] and Ahluwalia and Goyal [2], treatment processes for waste streams contaminated by metals include chemical precipitation, chemical oxidation or reduction, electrochemical treatment, membrane filtration, ion exchange, carbon sorption, and coprecipitation/sorption. These processes may be ineffective or extremely expensive when the metals in solution are in the 1–100 mg L^{-1} concentration range [3]. Alternative cost effective technologies or sorbents are needed for the treatment of metal-contaminated waste streams. A sorbent can be assumed to be "low cost" when it is abundant in nature, or when it is a by-product or waste material from another industry and requires little processing even when an improvement in sorption capacity compensates for the cost of additional processing. Natural materials available in large quantities, or certain waste products from industrial or agricultural operations may acquire potential as inexpensive sorbents. Due to their low cost, after being expended, they can be disposed of in landfills for hazardous waste disposal without any need for expensive regeneration or burned to recover the metal when its value is rewarding. Reviews have recently been published on the use of biomaterials (microbial [2], yeast [4] and algae [5] biomasses, chitosan [6]) as sorbents for the removal of heavy metals from wastewater. The potential of agricultural waste in removing a number of metal ions has been extensively reported. The use of agricultural by-products is an attractive opportunity as it combines the reuse of waste materials in the detoxification of wastewaters. From a first survey of the literature on ISI Web of Science looking for articles and reviews published from 1996 we can determine the most widely studied metal ions and biomasses, as well as the countries in which these studies were carried out. It is interesting to note that six metal ions account for 90% of these studies. These most widely studied metals are divalent cadmium, copper, zinc, nickel and lead followed by hexavalent and trivalent chromium (Fig. 1(left)). These metal ions have been studied much more than divalent mercury, iron, manganese, or trivalent iron. The types of studied biomasses are different and depended on the type of agricultural production prevailing in the geographical areas where the studies were carried out. An analysis of the literature shows the very wide distribution of countries where the ecological application of biomasses to metal removal is being developed, and indicates a great interest in emerging countries such as India, Brazil, Turkey, Argentina and Nigeria (Fig. 1(right)). Most of these studies are on a specific metal and only few of them make comparisons between sorbent affinities for different metal ions. Among them, Reddad et al. [7] and Saeed et al. [8] have compared the sorption of five different metals onto sugar beet pulp and black gram husk, respectively; Horsfall and Spiff [9], Montanher et al. [10] and Fiol et al. [11] have investigated the sorption of four different metals onto red pumpkin waste, rice bran and olive stones.

In some studies, the sorption of divalent metals and Cr^{3+} and Cr(VI) onto a specific sorbent was compared. Cimino et al. [12] studied the sorption of Cd^{2+}, Zn^{2+}, Cr^{3+} and Cr(VI) onto hazelnut shells and Sawalha et al. [13] the sorption of Cd^{2+} and Cr^{3+} and Cr(VI) onto saltbush leaves. In both studies the initial pH was in the 4.0–5.0 range for divalent metals and Cr^{3+} and the

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[1] In this paper sometimes we will make use of the "heavy metal" term, employed by and large in the reviewed environmental literature, even if we are aware that it lacks of a correct chemical meaning, as discussed by J.H. Duffus in his IUPAC Technical Report: "Heavy metals"—a meaningless term? (J.H. Duffus, Pure Appl. Chem. (2002) 74 793–807) "Over the past two decades, the term "heavy metals" has been widely used. It is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity. At the same time, legal regulations often specify a list of "heavy metals" to which they apply. Such lists differ from one set of regulations to another and the term is sometimes used without even specifying which "heavy metals" are covered. However, there is no authoritative definition to be found in the relevant literature. There is a tendency, unsupported by the facts, to assume that all so-called "heavy metals" and their compounds have highly toxic or ecotoxic properties. This has no basis in chemical or toxicological data. Thus, the term "heavy metals" is both meaningless and misleading. Even the term "metal" is commonly misused in both toxicological literature and in legislation to mean the pure metal and all the chemical species in which it may exist. This usage implies that the pure metal and all its compounds have the same physicochemical, biological, and toxicological properties, which is untrue. In order to avoid the use of the term "heavy metal", a new classification based on the periodic table is needed. Such a classification should reflect our understanding of the chemical basis of toxicity and allow toxic effects to be predicted".

pH was adjusted to 2.0 for Cr(VI). Studies of metal biosorption from binary or ternary mixtures are limited. For a better understanding of the main factors (pH, temperature, equilibrium parameters, etc.) that regulate sorption processes, this work presents an overview of the literature of the past 10 years on the use of a wide range of natural sorbents embodied in agriculture wastes in toxic metal ion removal.

2. Interaction between metal ions and biomasses

Volesky [14] divides the toxic metal ions into two groups: "the big three", i.e. mercury, lead and cadmium, and the "second-tier toxic heavy metals" that include copper, zinc, nickel, manganese, chromium, arsenic, selenium and vanadium. Many elements play a double role in the physiology of organisms; some are indispensable for normal life, while most of them are toxic at elevated concentrations, i.e. they adversely affect the activity and well-being of living organisms. In recent years there has been increasing concern on the potential toxic effects of metal ions that make up part of the products and by-products of our technologies [15]. In the following for each metal ion we report on its origin and toxicity, and present a table that shows literature results on metal ion-biomass interaction as presented in the original papers. In particular to describe the sorption process particle size, operative pH, temperature and Langmuir $q_{\max}$ are reported as significative parameters. In fact among the different isotherm models (Langmuir, Freundlich, Langmuir–Freundlich,...) used in literature to describe the sorption processes, Langmuir model is the simplest and generally used by the greatest part of authors. The parameter $q_{\max}$ represents the sorbent maximum capacity for a given metal ion and it is usually determined by fitting the isotherm experimental data to the Langmuir equation model:

$$q_{\mathrm{eq}} = \frac{q_{\max} b C_{\mathrm{eq}}}{1 + b C_{\mathrm{eq}}}$$

where q_{eq} is the amount of sorbate sorbed at equilibrium, C_{eq} the equilibrium concentration of sorbate in solution and b is the Langmuir constant related to the energy of sorption, which reflects quantitavely the affinity between the sorbent and the sorbate. The $q_{\max}$ values in the tables are always expressed as milligrams of sorbed metal ion respect to the weight in grams of dry sorbent.

2.1. Cadmium

The cadmium concentration in non-polluted natural water [16] is usually lower than 1 μg L^{-1}. The maximum acceptable cadmium in drinking water in E.U. regulations is 5 μg L^{-1}. In the past the main sources of cadmium were steel production, non-ferrous metal production, refining, cement manufacture, cadmium plating, battery manufacture, ashes from oil, waste and combustion, and phosphate fertilizers [17,18]. Nowadays, because of concerns about its environmental toxicity, the use of cadmium has 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 [19,20].

2.2. Copper

Copper pollution derives from copper mining, brass manufacture, electroplating industries and the use of copper compounds in agriculture. Copper is known as one of the highest mammalian toxic compounds [35]; inhalation of copper containing sprays is linked with an increase in lung cancer among exposed workers [36]. Copper sulphate is widely used as an algicide in water supply reservoirs affected by blooms of blue-green algae [37]. The maximum acceptable copper in drinking water in E.U. regulations is 1 mg L^{-1}.

2.3. Lead

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 [44]. 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 can reach water and soil through the corrosion of pipelines in water transportation systems and through the corrosion of paints. It cannot be broken down, but can be only converted to other forms. E.U. limit for lead in drinking water is 50 μg L^{-1}.

2.4. Zinc

Zinc and its products are widely used in alloy production, as anticorrosion coatings of steel and iron, in electrical devices, in rubber and tyre 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 metalloenzymes. Zinc is relatively nontoxic, even if daily doses greater than 100 mg during several months may lead to different disorders. This feature allows a high zinc limit in drinking water E.U. regulation (3 mg L^{-1}) [47].

2.5. Nickel

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 front of 8.5 million tonnes per year of nickel in the atmosphere due to natural sources, 43 million tonnes derive 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 [48]. The nickel content in surface water ranges from 2 to 20 $\mu g\,L^{-1}$ and E.U. limit concentration for nickel in drinking water is 50 $\mu g\,L^{-1}$.

2.6. Chromium

Chromium is a toxic metal of widespread use in many industries such as metal plating facilities, mining operations and tanneries. Chromium exists in water in a number of redox states, the most common being Cr(III), mainly as an aquo-ion, and Cr(VI), principally as chromate ion $CrO_4{}^{2-}$. The speciation of chromium has become of relevant interest in these last years because of the association Cr(VI)-cancer. The different toxicity of these two forms has been taken into account by EPA quality standards: 11 and 50 $\mu g\,L^{-1}$ for Cr(VI) and Cr(III), respectively. In oxygenated waters at $pH > 5$, Cr(VI) should be the predominant form according thermodynamic parameters; nevertheless several factors can influence the chromium redox speciation in water, as bacterial reduction, chemical reduction by Fe(II) in sediments or by dissolved oxidisable matter, stabilization of Cr(III) by complexation with dissolved organic ligands [49]. Cr(VI) is typically present as an anion and its direct precipitation is not an usual practice; the anionic species are instead usually reduced to trivalent state form and then precipitated as chromic hydroxide using lime. However, this method is only effective at high chromium concentrations and it presents several disadvantages such as a significant sludge production, an ever-increasing cost of landfill disposal and long-term environmental consequences.

2.7. General consideration

An analysis of q_{max} in Tables 1–7 shows a high variability not only among the different metal ions but also within the data for each of them. Before comparing these results we need to focus our attention on some outliers. Disregarding the values with saltbush leaves [13], which look affected by some gross mistake in the units used (1 g of saltbush that sorbs 2.5 g of Cd^{2+} is an extraordinary result, but that Amberlite IR-120 resin can sorb 201.0 mol Cd^{2+} per gram, i.e. 22.59 kg/g, is practically a miracle), the values for Cd^{2+} reported by Benaïssa [32] seem particularly high. An inspection of the isotherms in Fig. 10 of Ref. [32] shows that the q_{max} for peas peel, medlar peel and fig leaves surely does not exceed 92 mg/g and for broad bean peel of about 120 mg/g, compared to the values of 118.91, 98.14, 103.09 and 147.71 reported in Table 4 of the same reference. Evidently the linearization procedure must have introduced a very large error amplification which could have been avoided by a simple visual inspection of the plot. The q_{max} values reported in the tables are therefore 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+}. 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+}, these values look more similar and the

Table 1
Cadmium sorption by some agricultural wastes

Sorbent	Particle size	pH	°C	q_{max} Langmuir (mg/g)	Reference
Papaya wood	0.05–0.2 mm	5	n.d.	17.22	[21]
Green coconut shell	Powder	7	27	285.7	[22]
Hazelnut shells	0.3–0.8 mm	4	n.d.	5.42	[12]
Juniper fiber	Powder	n.d.	n.d.	9.2	[23]
Black gram husk	1–4 mm	5	25 ± 2	38.78	[24]
Sugar beet pulp	0.25–0.50 mm	5.5	20.0 ± 0.5	24.39	[7]
Fluted pumpkin	<100 mesh	5	n.d.	3.79	[25]
Kudzu	420–710 × 10^{-3} mm	n.d.	n.d.	15	[26]
Cassava	<100 mesh	4.5	n.d	n.d.	[27]
Pang Da Hai	60–50 mesh	6.5	25	17.5	[28]
Rice bran	150–425 × 10^{-3} mm	5	25 ± 1	n.d.	[10]
Grape stalks	1–1.5 mm	5.5	25	27.88	[29]
Pinus sylvestris sawdust	0.1–0.25 mm	4	20.5 ± 0.5	15.27	[30]
Pinus sylvestris sawdust	0.1–0.25 mm	5	20.5 ± 0.5	19.08	[30]
Pinus sylvestris sawdust	0.1–0.25 mm	7	20.5 ± 0.5	6.72	[30]
Black gram husk	n.d.	5	25 ± 2	39.99	[8]
Brazil nut shells	100–250 μm	5.8	28 ± 1	19.4	[31]
Stems of A. donax	100–250 μm	5.8	28 ± 1	5.7	[31]
Sugarcane bagasse	100–250 μm	5.8	28 ± 1	10.7	[31]
P. ruscifolia wood	100–250 μm	5.8	28 ± 1	7.4	[31]
Saltbush leaves	0.149 mm	5	24 ± 2	2490	[13]
Peas peel	0.50–0.8 mm	7	25 ± 1	118.91	[32]
Broad bean peel	0.50–0.8 mm	7	25 ± 1	147.71	[32]
Medlar peel	0.50–0.8 mm	7	25 ± 1	98.14	[32]
Fig leaves	>0.125 mm	7	25 ± 1	103.09	[32]
Cassava waste	100 mesh	5.0	n.d.	n.d	[33]
Juniper trees	<3 mm	5.0 ± 0.1	25	2.81	[34]

Table 2
Copper sorption by some agricultural wastes

Sorbent	Particle size	pH	°C	$q_{\max}$ Langmuir (mg/g)	Reference
Papaya wood	0.05–0.2 mm	5	n.d.	19.88	[21]
Tree fern	78–88 × 10^{-3} mm	n.d.	40	11.7	[38]
Olive mill	Variable	4	23	5.0	[39]
Olive mill	Variable	5	23	13.5	[39]
Sugar beet pulp	0.25–0.50 mm	5.5	20.0 ± 0.5	21.16	[7]
Cork biomass	50–100 × 10^{-3} mm	6	25	21[a]	[40]
Kudzu	420–710 × 10^{-3} mm	n.d.	n.d.	32.00	[26]
Cassava	<100 mesh	4.5	n.d	n.d.	[27]
Rice bran	150–425 × 10^{-3} mm	5	25 ± 1	n.d.	[10]
Pepper paste	300 × 10^{-3} mm	5	20	16.71	[41]
Pepper paste	300 × 10^{-3} mm	5	30	19.07	[41]
Pepper paste	300 × 10^{-3} mm	5	40	24.97	[41]
Pepper paste	300 × 10^{-3} mm	5	50	28.41	[41]
Plant leaves	1 mm	n.d	n.d.	n.d.	[42]
Black gram husk	n.d.	5	25 ± 2	27.73	[8]
Sugar beet pulp	0.25–0.5 mm	4	20.0 ± 0.5	23	[43]
Sugar beet pulp	0.25–0.5 mm	6	20.0 ± 0.5	27	[43]

[a] Saturation experimental value.

Table 3
Lead sorption by some agricultural wastes

Sorbent	Particle size	pH	°C	$q_{\max}$ Langmuir (mg/g)	Reference
Sugar beet pulp	0.25–0.50 mm	5.5	20.0 ± 0.5	73.76	[7]
Rhizophora mangle	100 × 10^{-3} mm	5	n.d.	31.25	[45]
Fluted pumpkin	<100 mesh	5	n.d.	9.54	[25]
Pang Da Hai	60–50 mesh	6.5	25	27.1	[28]
Rice bran	150–425 × 10^{-3} mm	5	25 ± 1	n.d.	[10]
Grape stalks	1–1.5 mm	5.5	25	49.93	[29]
Pinus sylvestris sawdust	0.1–0.25 mm	4	20.5 ± 0.5	15.77	[30]
Pinus sylvestris sawdust	0.1–0.25 mm	5	20.5 ± 0.5	22.22	[30]
Pinus sylvestris sawdust	0.1–0.25 mm	7	20.5 ± 0.5	8.45	[30]
Black gram husk	n.d.	5	25 ± 2	49.97	[8]
Chaff	104–120 × 10^{-3} mm	5.5	20	12.5	[46]
Chaff	104–120 × 10^{-3} mm	5.5	25	11.9	[46]
Chaff	104–120 × 10^{-3} mm	5.5	30	10.4	[46]
Sugar beet pulp	0.25–0.5 mm	4	20.0 ± 0.5	50	[43]
Sugar beet pulp	0.25–0.5 mm	6	20.0 ± 0.5	57	[43]

maximum quantity of metal ion sorbed by a gram of sorbent is of the order of 0.5 mmol (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.). The use of chemical (mmol/g) instead of technical (mg/g) units has to be recommended whenever comparisons have to be made, as can be argued from the above considerations. The use of chemical units allows to better characterize the behaviour of a given sorbent: the results obtained in this way contain in fact information on

Table 4
Zinc sorption by some agricultural wastes

Sorbent	Particle size	pH	°C	$q_{\max}$ Langmuir (mg/g)	Reference
Papaya wood	0.05–0.2 mm	5	n.d.	13.45	[21]
Hazelnut shells	0.3–0.8 mm	4	n.d.	1.78	[12]
Sugar beet pulp	0.25–0.50 mm	5.5	20.0 ± 0.5	17.78	[7]
Cork biomass	50–100 × 10^{-3} mm	6	25	25[a]	[40]
Fluted pumpkin	<100 mesh	5	n.d.	13.33	[25]
Kudzu	420–710 × 10^{-3} mm	n.d.	n.d.	35	[26]
Cassava	<100 mesh	4.5	n.d	n.d.	[27]
Rice bran	150–425 × 10^{-3} mm	5	25 ± 1	n.d.	[10]
Black gram husk	n.d.	5	25 ± 2	33.81	[8]
Cassava	100 mesh	5	n.d.	n.d	[27]

[a] Saturation experimental value.

Table 5
Nickel sorption by some agricultural wastes

Sorbent	Particle size	pH	°C	$q_{\max}$ Langmuir (mg/g)	Reference
Sugar beet pulp	0.25–0.50 mm	5.5	20.0 ± 0.5	11.85	[7]
Cork biomass	50–100 × 10^{-3} mm	6	25	10.5[a]	[40]
Black gram husk	n.d.	5	25 ± 2	19.56	[8]
Brazil nut shells	100–250 μm	5.8	28 ± 1	7.9	[31]
Sugar beet pulp	0.25–0.5 mm	4	20.0 ± 0.5	11	[43]
Sugar beet pulp	0.25–0.5 mm	6	20.0 ± 0.5	12	[43]

[a] Saturation experimental value.

Table 6
Chromium(VI) sorption by some agricultural wastes

Sorbent	Particle size	pH	°C	$q_{\max}$ Langmuir (mg/g)	Reference
Tea factory waste	0–15–0.25 mm	2	25	27.24	[50]
Tea factory waste	0–15–0.25 mm	2	45	36.9	[50]
Tea factory waste	0–15–0.25 mm	2	60	54.65	[50]
Hazelnut shells	0.3–0.8 mm	2	n.d.	17.2	[12]
Agave lechuguilla	n.d	2	10	92.3	[51]
Agave lechuguilla	n.d.	2	22	123.08	[51]
Agave lechuguilla	n.d.	2	40	126.92	[51]
Saltbush leaves	0.149 mm	2	24 ± 2	410	[13]
Thuja orientalis cones	125–250 × 10^{-3} mm	1.5	16	48.8	[52]

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 the literature cited for each metal ion, different variables (particle size, temperature, pH, exchange and so on), kinetics and thermodynamic (Langmuir, Freundlich, etc.) models are taken into account. In the following sections we will discuss in detail the effect of the pH and temperature on the sorption processes. As far as regards the thermodynamic model used, the capacity of a given biomass to absorb toxic metals has been traditionally quantified using the Langmuir, Freundlich, Langmuir–Freundlich isotherms, or different alternative models. These isotherms were developed under assumptions that are generally not met in biosorption processes. The main reason for their extended use is that they describe experimental data satisfactorily. They can be used for predictions, although they do not take into account external parameters, such as the pH or ionic strength.

Another important parameter studied was the influence of the particle size. This plays an important role in determining cost of the process. The results presented in Tables 1–7 clearly show that this parameter has not been studied systematically and each author uses his own proper conditions. It is important to stress that in a general way smaller particles should favour sorption processes, even though, according to Leusch and Volesky [53] larger particles with spherical shapes can give higher metal sorptions which is attributed to mass transport inside the sorbent particles.

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 using several variables, i.e. sorbate and sorbent concentration, agitation speed, particle size, temperature, etc., and to fit the data to different kinetic models in order to confirm whether the mechanism is film diffusion, kinetic sorption, diffusion sorption or a combination of these processes. The most widely used kinetic models in biosorption studies have been revised by Ho et al. [54].

3. Effect of the pH on sorption

3.1. State of the art

The pH of metal solutions has been identified as the most important variable governing metal sorption [55]. When designing a process for metal removal from wastewater, both optimal pH value for metal sorption and pH value required for effluent discharge to comply with regulations must be taken into consideration before making a final decision. For divalent metal sorption different authors have found that sorption increases with the pH and have reported that it was most efficient at pH

Table 7
Chromium(III) sorption by some agricultural wastes

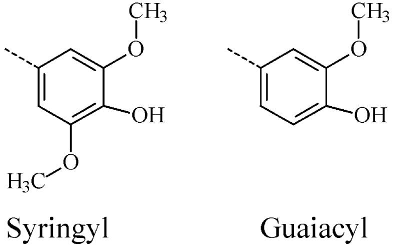
Sorbent	Particle size	pH	°C	$q_{\max}$ Langmuir (mg/g)	Reference
Hazelnut shells	0.3–0.8 mm	4	n.d.	3.08	[12]
Saltbush leaves	0.149 mm	5	24 ± 2	1730	[13]

values of around 5. Optimal removal at pH 5.0 for different divalent metals has been reported for papaya wood, black gram husk, nuts shells, saltbush biomass, cassava waste and rice bran [8,21,24,31,13,33,10]. In his study Reddad et al. [7] found an optimal pH of 5.5 for sugar beet pulp, which value was also found as optimal for pumpkin [9], grape stalks [29], olive stones [11] and chaff [46]. A higher pH value (7.0) was used for a cadmium sorption investigation on sawdust of *Pinus sylvestris* [30], peas peel [32], broad bean [32], medlar peel [32], fig leaves [32] and coconut shell [22].

However, the sorption of metal anions like Cr(VI) is found to increase when decreasing the pH to acidic values. Low pH values within the 2–3 range have been found to be favourable to Cr(VI) biosorption. Within the 1.0–4.0 pH range $HCrO_4^-$ and CrO_4^{2-} are the major species in solution and their stability depends on the pH and the hexavalent chromium concentration. At low pH the active sites of the biosorbent are protonated and these anionic species can be bound on the sorbent by electrostatic forces. Maximum uptake values of Cr(VI) were observed at pH 2.0 for tea waste [50], hazelnut shells [12], *Agave lechuguilla* [51], saltbush [13], yohimbe bark [56] and olive stones [11]. In other studies, pH 3.0 and 1.5 were found to be optimal for the hexavalent chromium sorption onto cork and grape stalks [56], and Thuja orientalis [52], respectively.

3.2. Sorption mechanism investigation

The real challenge in the field of biosorption is to identify the mechanism that govern metal uptake by biosorbents. One of the mechanisms involved in the sorption of positively charged metal species is the ion-exchange process between protons/or alkaline and alkaline earth metals as counterions present in the biomass and metal ions taken up from water [57]. 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 [58]) can be viewed as natural ion-exchange materials that primarily contain weak acidic and basic groups on the surface. In the 2.5–6.0 pH range the binding of heavy metals is determined by the degree of dissociation of the weakly acidic groups. This kind of mechanism is normally investigated by analyzing the release of alkaline and alkaline earth metal ions during the sorption process. The release of K^+, Mg^{2+} and Ca^{2+} has been accounted to determine the extent of ion exchange mechanism taking place in heavy metal removal by grape stalks waste [29,59], yohimbe bark [60] and olive stone waste [11]. Gérente et al. [43], who measured simultaneously the release of calcium ions during the sorption of different divalent metals on sugar beet pulp, found that the mode of fixation was 100%, 95% and 75% by ion exchange for nickel, copper and lead ions, respectively. Sorption was reported to be the additional sorption mechanism for copper and lead ions. Sugar beet pulp was also used as a sorbent of heavy metals by Reddad et al. [7]. In this work the reported ion exchange mechanism percentages were 100%, 90%, 78%, 60% and 58% for nickel, cadmium, zinc, copper and lead, respectively. Additional metal ion sorption was reported to be due to the complex formation of metal ions with the biosorbent functional groups. The functional groups on the sorbent surface that may involve metal ion sorption are usually investigated by Fourier Transform Infrared (FTIR) Spectroscopy. In some recent studies, the existence of ion exchange between light metal ions on the sorbent surface and heavy metals in solution was confirmed by Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX). This technique was used to confirm ion exchange between cadmium ions in solution and calcium on the surface of husks of *Lathyrus sativus* [61] and to determine that microprecipitation of metal ions takes place on the surface of the sorbent. The exchange of light ions on the particles of green coconut shell with cadmium ions was also investigated by SEM-EDX analysis [22]. Ion exchange mechanism for copper sorption onto yohimbe bark was also confirmed by SEM-EDAX analysis [59]. Villaescusa et al. [62] and Nurchi et al. [63] applied ^{13}C CP-MAS NMR to the elucidation of the interaction of Cu^{2+} and Ni^{2+} with cork wastes and of Cu^{2+}, Cd^{2+} and Ni^{2+} with olive stones. NMR signal analysis suggested a specific metal complexation on the carbohydrate moieties of the polymeric cork matrix in the first work, and a complexation between metal ions and hydroxyl groups on the guaiacyl and syringyl moieties in the second.



3.3. Potentiometry

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. Based on the content of functional groups on sugar beet pulp, Reddad et al. [7] determined the content of carboxyl and phenol moieties by potentiometric titration and then applied a surface complexation model based on the diffuse layer model to describe the sorption of Cu^{2+}, Zn^{2+}, Cd^{2+} and Ni^{2+} ions. Komy [64] used potentiometric and conductimetric titrations to describe the protonation of cumin biomass and the reactivity of its surface to adsorb Cu^{2+} and Zn^{2+} ions. Thanks to potentiometric titrations of untreated and copper- and nickel-treated cork samples it was possible to distinguish two kinds of interactions: a strong one that involves protonated sites on cork and a weaker one that allows hydroxide precipitation of the bound metal ion into the cork structure [62].

3.4. pH effects on metal ion hydrolysis and coordination

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 absorbing material on the pH;
3. dependence of the interaction metal ion-sorbent on the pH.

As pointed out by Baes and Mesmer [65] 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 the distribution diagrams of the possible hydroxo-soluble species were obtained for Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} using the formation constants reported by Baes and Mesmer with the Hyss2006 program [66]. With this program the distribution plots can be calculated taking into account also the formation of the insoluble hydroxides.

Fig. 2 shows the species distribution diagrams for a metal concentration of 100 mg L^{-1} (very high polluting concentration, which corresponds to molar concentrations ranging from 0.48 mM for lead to 1.92 mM for chromium) and the diagrams for the E.U. limit concentration (which take into account the different toxicities) in water for human use.

Besides the immediate observation of an appreciable difference between distribution diagrams at the two concentrations for all metal ions, these plots also allow further considerations:

- In the case of Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} at 100 mg L^{-1}, the increase in pH does not produce soluble species different from the aquo-ions until precipitation (pH ~ 5 copper–pH ~ 8.5 cadmium).
- At 100 mg L^{-1} before hydroxide precipitation at pH ~ 6, Cr^{3+} gives almost quantitatively the polynuclear species $Cr_3(OH)_4{}^{5+}$ (pH ~ 3) besides the minor species $Cr(OH)^{2+}$, $Cr_2(OH)_2{}^{4+}$ and $Cr(OH)^{+}$.
- In the case of lead 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 at pH ~ 9.5.
- At the lower concentrations corresponding to E.U. limits, Cu^{2+}, Ni^{2+} and Zn^{2+} exhibit the same behaviour as above, shifted at a higher pH.
- The very low concentration E.U. limits for cadmium (5 μg L^{-1}) prevents hydroxide precipitation and various mononuclear species appear progressively.
- At 50 μg L^{-1}, Pb^{2+} and Cr^{3+} 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 acido–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. In this simplifying 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.

We calculated the distribution plot, using the literature constants in Table 8 (Fig. 3A) for a solution containing Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} each at 100 mg L^{-1} (corresponding to 1.51, 1.7, 1.53, 0.89 and 0.48 mM, respectively) in contact with the amount of solid particles containing enough “*salicylic*” groups to coordinate all metal ions in a 1:1 mode (*salicylate* 6.17 mM)). In the same way we calculated the distribution plot in excess of *salicylate* groups (12.34 mM) and in defect of the same (3.08 mM) (Fig. 3B and C, respectively).

These plots allow a few considerations:

- Each metal ion has a proper trend with the pH which depends on the binding strength and not directly on the ionization properties of the binding groups.
- Lead and cadmium ions would give precipitation before being coordinated.

Table 8
log β of protonation and formation constants of 1:1 complexes with salicylate

Formed compound	log β	References
SalH	13.40	[67]
$SalH_2$	16.22	[67]
CuSal	10.04	[68]
NiSal	8.41	[69]
ZnSal	7.83	[70]
CdSal	5.1	[71]
PbSal	5.9	[71]

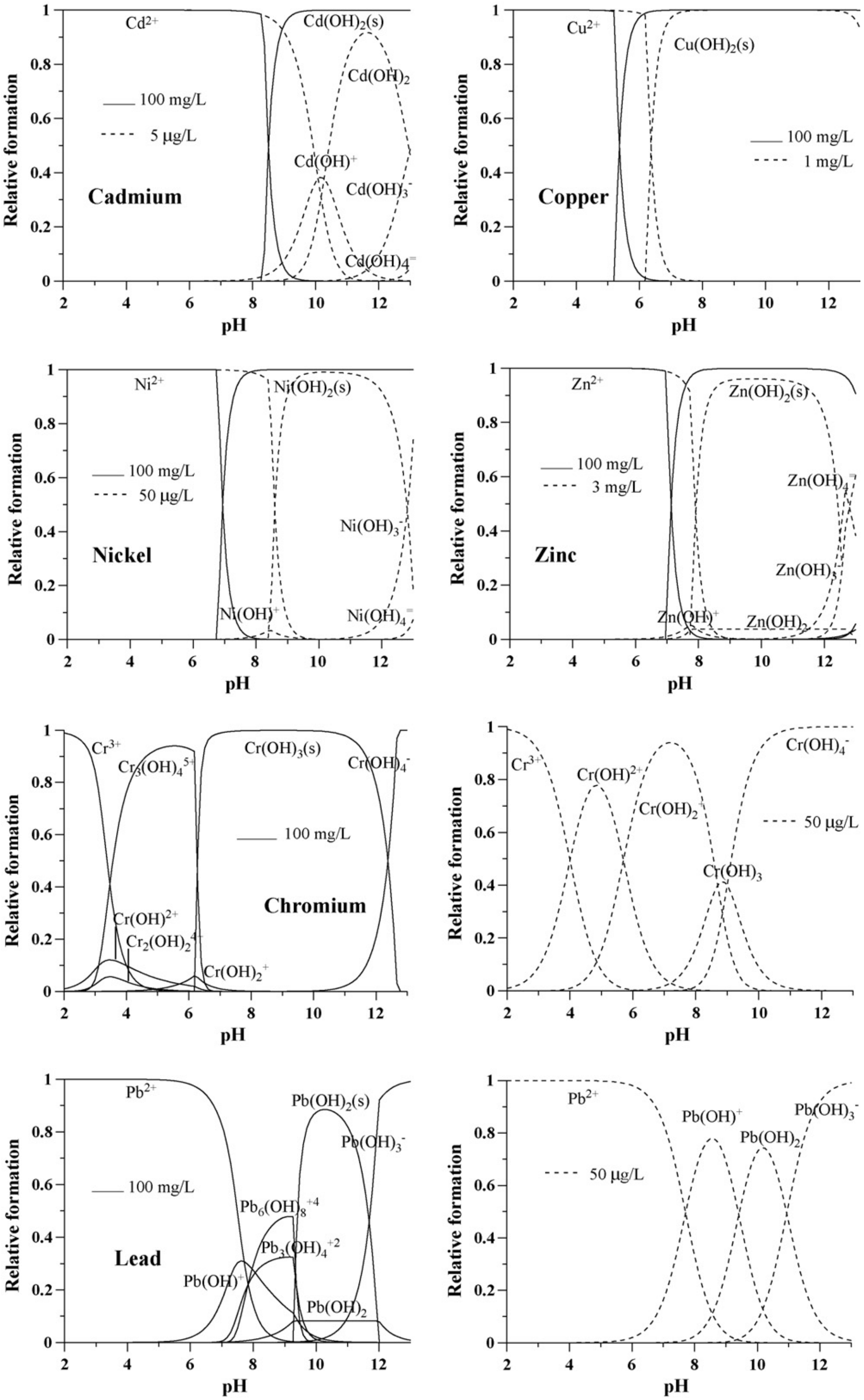


Fig. 2. Species distribution diagrams for a metal concentration of 100 mg L^{-1} (continuous lines) and diagrams for the E.U. limit concentration (dotted lines).

- The trend with the pH is strictly related to the concentrations of the binding group.
- Competition between metal ions for the same coordinating group takes place when the amount of chelating groups is less than the stoichiometric requirement.

4. Effect of temperature

Most studies on metal ion sorption on agricultural wastes have been carried out at a fixed temperature in the 20–25 °C range [72,7,43]. Nevertheless, Ho [38] studied copper sorption on tree

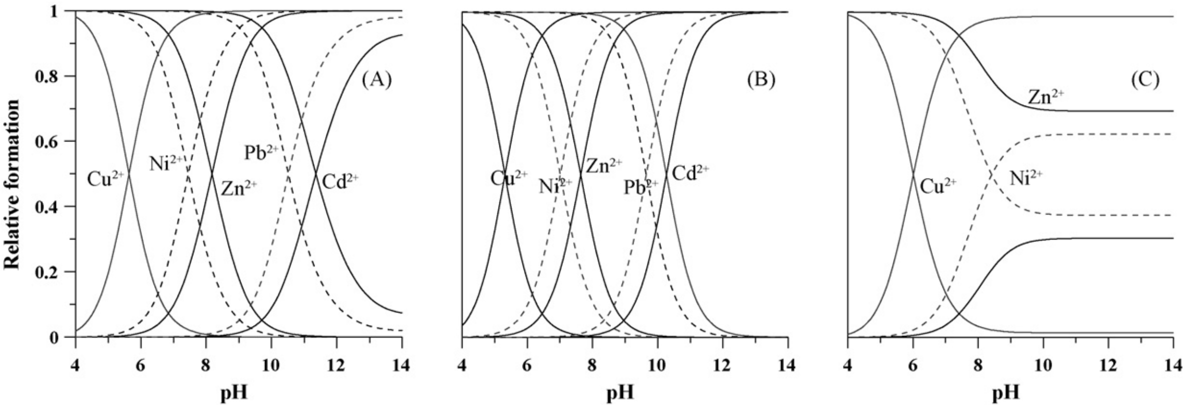


Fig. 3. Distribution plot calculated with the Hyss2006 program for a solution containing Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} each at 100 mg L^{-1} (corresponding to 1.51, 1.7, 1.53, 0.89 and 0.48 mM, respectively) in contact with the amount of solid particles containing "*salicylic*" groups (A) 6.17 mM, (B) 12.34 mM and (C) 3.08 mM. Each metal distribution was normalized according to its own total concentration.

fern at 40 and 30 °C, and 28 ± 1 °C was the temperature chosen by Panda et al. [61] and Basso et al. [31] to study cadmium sorption on husk of *Lathyrus sativus* and cadmium and nickel sorption on Brazil nut shells, respectively.

The temperature could be a parameter that affects the sorption of metal ions. However, most reported studies on metal ion sorption on biomasses conclude that the influence of temperature is to a limited extent and only in a certain temperature range. This fact indicates that ion exchange is one of the mechanisms responsible for the sorption process [73]. It has been reported [74] that biosorption reactions are normally exothermic which indicates that sorbent capacity increases with decreasing temperature. Han et al. [46] found that an increase in temperature from 20 to 30 °C resulted in a slightly lower lead load per unit weight of chaff, an agriculture by-product harvested in China as feed for livestock and poultry. Conversely, sorption of Cu^{2+} on *Capsicum annuum* seeds, one of the by-products from the waste of a pepper paste factory was found to be favoured with an increase in temperature in the 20–50 °C range [41]. Romero-González et al. [51] also found that the sorption capacity of *Agave lechuguilla* leaves, a plant of the Chihuahuan desert, for Cr(VI) sorption increased on increasing the temperature in the 10–40 °C range. The authors justify the endothermicity of the process with the apparent binding and reduction of Cr(VI) to Cr^{3+}. Malkoc and Nuhoglu [50] also found that the process of Cr(VI) sorption on tea factory waste is endothermic and metal uptake increases on increasing the temperature from 25 to 60 °C. The favourable effect of temperature on sorption may be a result of a swelling effect within the internal structure of the sorbent enabling large metal ions like Cr(VI) to penetrate further.

5. Conclusions

As a final remark we would like to point out the general difficulty in comparing the results from works performed under very different experimental conditions. Nevertheless, we would also like to mention some positive aspects in recent studies:

- Sorption studies are generally performed with comparable procedures.
- Some effects of the factors affecting the sorption process such as particle size, pH, metal ion concentration, agitation time, and kinetics are often taken into consideration.

Some further suggestions to authors working in this field could be:

- ○ to examine the above factors more systematically;
- ○ since the Langmuir (or Freundlich) isotherm is sufficient to describe the behaviour of the system, the use of more complex models should be avoided, unless justified by the fact that additional information is obtained;
- ○ the calculation of isotherm parameters from linearized forms nowadays is not a necessity, and non-linear least squares calculations on original data can be performed easily.

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