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Valorisation of Lignocellulosic Biomass Wastes for the Removal of Metal Ions from Aqueous Streams: A Review

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Additional information is available at the end of the chapter

Abstract

Heavy metal pollution derived from anthropogenic activities is a relevant environmental threat nowadays due to their toxic nature, persistence and accumulation potential in the food chain. A wide variety of lignocellulosic-based biomaterials have been thoroughly assessed by the scientific community as sorbents for the removal of metals from aqueous streams. This kind of biomaterials, mainly constituted by lignin and cellulose, bear functional groups such as alcohol, ketone and carboxylates that provide active sorption points for the effective removal of heavy metals. The role of lignin in the sorption process is especially relevant, since this substance provides polyhydroxy and polyphenol functional groups—especially effective in the coordination of metals—and that provide ion exchange functionality to the material. Depending on their nature, these materials can be used either in their raw form or chemically modified form so as to enhance their sorption capacity and/or to achieve improved mechanical and mass transfer properties.

Keywords: lignocellulosic wastes, immobilisation, heavy metals, sorption, desorption, kinetics, equilibrium, modelling, recovery

1. Introduction

1.1. Heavy metal pollution

Heavy metals occur as natural constituents of the earth crust and some of them considered as persistent environmental pollutants. They may vary in oxidation state and hydrochemical

speciation, but cannot be degraded or destroyed. The problems related to heavy metal pollution are transversal; water, air and soil components are susceptible of being severely polluted [1].

To a large degree, industrial activities are mainly responsible for environmental discharges and pollution. There are many industrial sources of pollution including manufacturing processes such as smelting and refining, electricity generation and nuclear power, agricultural fertilisation, wastewater treatment, fuel combustion, production of batteries, alloys manufacturing, electroplating, waste incineration, ceramics production and glass colouring [2].

Human exposure and intake of hazardous levels of heavy metals may occur through food, air and water [1]. It should be highlighted as well that some metals such as barium, cadmium, chromium, mercury, lead and hazardous metalloids such as arsenic can be bioaccumulated in different organs and may exert their toxic effects after long time of periodic ingestion of even low levels.

1.2. Structure of lignocellulosic biomass

Lignocellulosic biomass has been pointed out as a valuable source of chemicals and materials for different applications and a very relevant actor in the design of strategies to reduce the social and economic reliance on fossil resources. These materials are naturally produced from incorporation of CO_2 and water (driven by solar power) through the photosynthesis process. In this context, lignocellulosic biomass is the most abundant and biorenewable biomass on earth [3].

The major components of these materials are cellulose, hemicellulose and lignin, and cellulose and hemicellulose are considered to be polysaccharides. The structure of cellulose is based on the molecular formula $(C_6H_{10}O_5)_n$ and is one of the most relevant polysaccharides occurring in the plant cell wall. Hundreds of glucose units are linked through glucosidic linkage (**Figure 1a**) and individual chains usually interact with one another through hydrogen bonds. This material has found an extensive use in the paper industry. Hemicellulose is another important polysaccharide usually contained in lignocellulosic biomass with a more intricate structure and linkages than cellulose. Hemicellulose is composed of heteropolymers and may contain xyloglucan, xylan, glucomannans and galactoglucomannans in variable ratios depending on the type of biomass.

When it comes to heavy metal sorption by raw, unmodified lignocellulosic biomass, lignin has been found to play a key role. Lignin is a three-dimensional structure made of phenolic polymers that consists of three types of phenylpropanoid units: *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (**Figure 1b**). A short section of a lignin polymer is presented in **Figure 1(c)**. This substance acts as cellular glue, joining the individual fibres and conferring strength to the plant tissue. The richness in electron-donor active sites that are provided in the polyhydroxy and polyphenol functional groups of lignin offers a unique frame for the interaction and binding of cationic heavy metals [6].
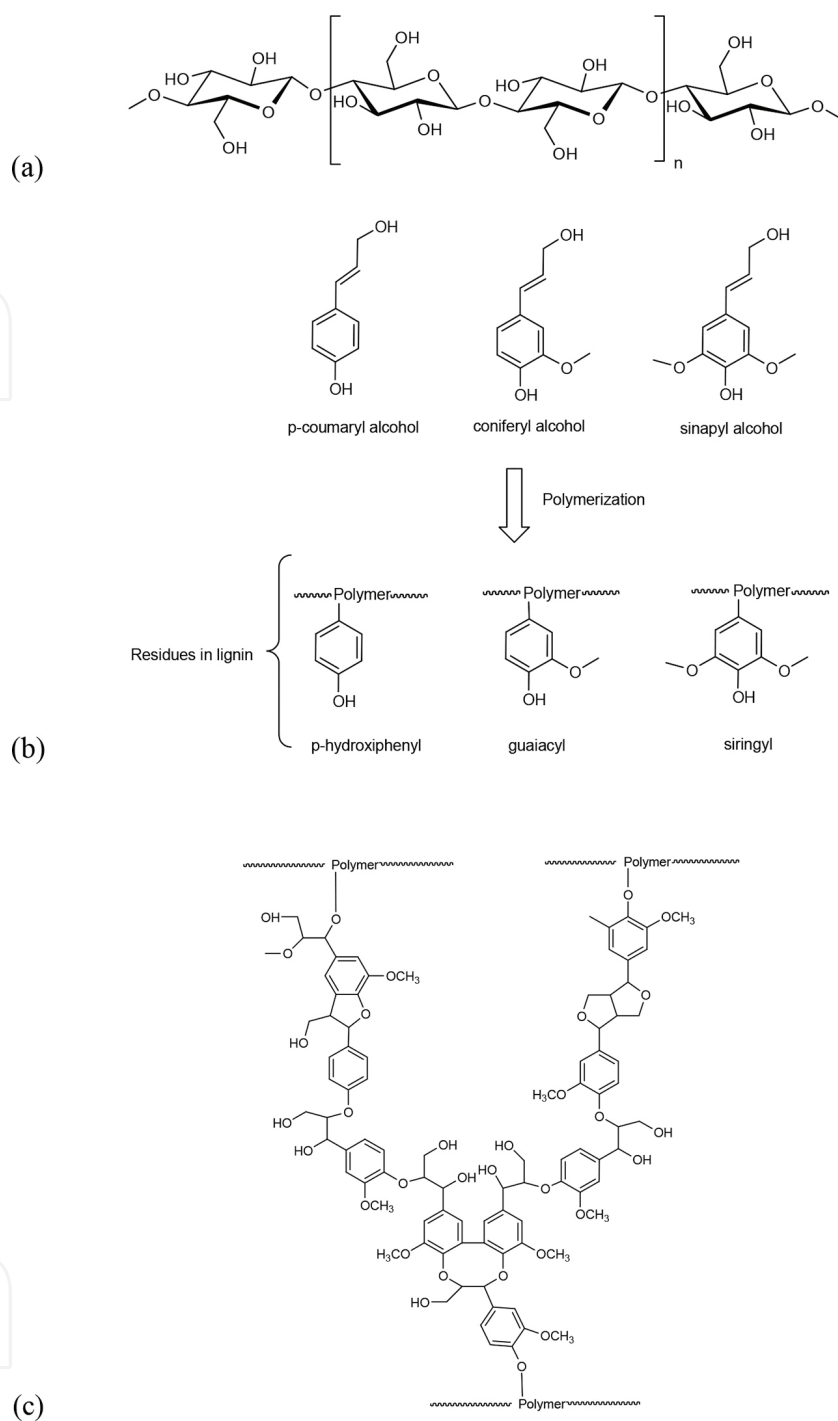
Figure 1. Structure of (a) cellulose, (b) main phenylpropane units and their related residues found in lignin and (c) structure of a lignin template [4, 5].

Abdolali et al. reported the chemical composition of some common lignocellulosic materials studied in metal sorption processes [6]. In general terms, lignocellulosic sorbents are composed of cellulose (30–35%), hemicellulose (20–40%), lignin (15–25%) and small amounts of water, ash, cyclic hydrocarbons and extractives. The chemical compositions in lignocellulosic materials are in different percentages depending on plant and also on the part of plant: leaves

contain lower percentage of cellulose (15–25%) and lignin (5–10%) but higher percentage of hemicellulose (70–80%), while in stones and nuts, the lignin content is higher than cellulose and hemicellulose (30–40%). Pujol et al. reported a composition of about 25% total lignin and 23% polysaccharides in exhausted coffee wastes [7]. They also reported a relative composition depending on the particle size when characterising the different components of grape stalks (GS) [8].

The main constituents of lignocellulosic materials contain a variety of functional groups that play an important role in metal sorption. It was reported that acetamido groups, carbonyl, phenolic, structural polysaccharides, amino, amido, sulphydryl, carboxyl groups, alcohol and esters, present in lignocellulosic materials have affinity for metal complexation [9]. Ion exchange between positive cations and sodium, potassium, calcium and magnesium present in the adsorbent was identified as an important mechanism in several studies. These two mechanisms, together with chelation, are the main mechanisms known for metal sorption in lignocellulosic sorbents [9].

2. Lignocellulosic-based materials for the removal of heavy metals from aqueous effluents

Lignocellulosic materials from agricultural or plant wastes have been widely studied due to their renewable nature, large production and great local availability. A review of the recent literature reveals that hundreds of lignocellulosic materials around the world were tested to be used as low-cost sorbents for heavy metals and most of them are considered efficient and promising sorbents. The only negative aspects related to the use of raw lignocellulosic materials are connected to the lower sorption capacity compared to activated carbons and commercial ion exchange resins, as well as the potential release of organic matter that might cause a secondary pollution in the water treated.

Recently, Malik et al. reviewed low-cost adsorbents from different plant parts: husks, shells, straws, stems and woods, leaves, barks, grasses, stalks, seeds and hulls, fibres, fruit peels and pulps, bagasse and other lignocellulosic-based materials such as corn cob, oaks or fruit stones to be used as biosorbents [10]. The particular physicochemical properties of each material determine its properties as a sorbent.

Metal sorption by these heterogeneous materials is a complex process affected not only by the main mechanism, but also by other secondary mechanisms and combinations of different phenomena including chemisorption, adsorption on surface pores, adsorption by physical forces, entrapment in inter- and intra-fibrillar capillaries and spaces of the structural polysaccharides network, diffusion through cell walls and membranes, surface precipitation and metal reduction [9, 11]. The main mechanisms involved in the interaction between a specific sorbent material and metals could be predicted and verified by combination of different spectroscopic techniques and conventional techniques such as titration, chemical blocking of functional groups and related release of cations from sorbent [6].

The efficiency of each sorbent extremely depends on the operating conditions such as temperature, sorbent particle size, pH, contact time or initial metal concentration. For this reason, a thorough study to find out the optimal sorption conditions is required for each couple sorbent metal. Hundreds of these studies can be found in the literature, where the optimal conditions for a specific pair of lignocellulosic sorbent metal were reported. The main results in this field can be found in reviews published in prestigious journals, helping the researchers to update the information about potential biosorbents suitable for a given application [6, 9, 11–14]. In these reviews, the performance of different types of lignocellulosic sorbents is usually expressed as maximum sorption capacity (q_{max}) and the efficiency comparison between materials used to be based in these values. Nevertheless, additional information is needed to compare sorption efficiency between sorbents for a specific metal due to differences in particle sorbent sizes, sorbent dosages and other experimental conditions used in each work.

A large share of current research on metal sorption by lignocellulosic materials has focused on the removal of heavy metal cations, such as Pb(II), Cd(II), Zn(II) and Cu(II) [4], but other toxic metals such as Ni(II), Al(III), Hg(II), Fe(II), chromium and metalloids (arsenic, selenium, molybdenum, and vanadium) have been also studied as target pollutant in biosorption processes [15].

Nowadays however, there is a growing interest in biosorption processes that use low-cost materials as sorbents for the recovery of rare earths or precious metals [16, 17]. The recovery of valuable metals by biosorption opens a challenging and exciting new scenario in sorption studies far beyond the regular water treatment, since the recovered material is expected to have an intrinsic economic value.

Despite metal sorption using biomass has been regarded as an environmental-friendly technique and provides a set of potential advantages against traditional technologies; most of the studies have been focused on synthetic solutions. To the best of our knowledge, studies reporting the use of biosorption-based technologies for metal removal from real scenarios of contaminated wastewaters are scarce. Few studies have so far explored the use of lignocellulosic materials in the treatment of real polluted wastewater. Fruit shell of gulmohar and olive stones were investigated for the removal of Cr(VI) from an electroplating wastewater [18, 19], and rice agro-wastes, coconut shell, neem leaves and hyacinth roots were used for the removal of Pb(II) from wastewater in a battery industry [20], and recently Liu et al. [21] published a complete method for chromium electroplating wastewater treatment based on biosorption using exhausted coffee.

3. Structural characterisation of lignocellulosic wastes and their interactions with heavy metals

3.1. Infrared spectroscopy

Infrared spectroscopy (IR) is a technique based on the vibrations of the atoms on a given molecule and is a result of the molecular vibration mechanism, which refers to energy-matter

interaction [22]. Usually, an infrared spectrum is obtained by passing infrared radiation through a sample and quantifying the fraction of incident radiation of each frequency that has been absorbed. The energy at which a peak appears in an absorption (or transmission) spectra corresponds to the characteristic energy of the vibration in a part of the molecule. The selection rule for IR spectroscopy is that an electric dipole moment in the molecule has to change during the vibration.

Techniques based on IR spectroscopy have become a powerful tool for determining the functional groups and the mechanisms involved in the removal of heavy metals by different type of biomass. A magnification in the region 800–1800 cm^{-1} of a raw lignocellulosic material (grape stalk wastes) and exposed to either Cr(III) or Cr(VI) solutions are presented in **Figure 2**. In the spectra, the positions of the main bands that have suffered modifications in their frequencies have been indicated with arrows.
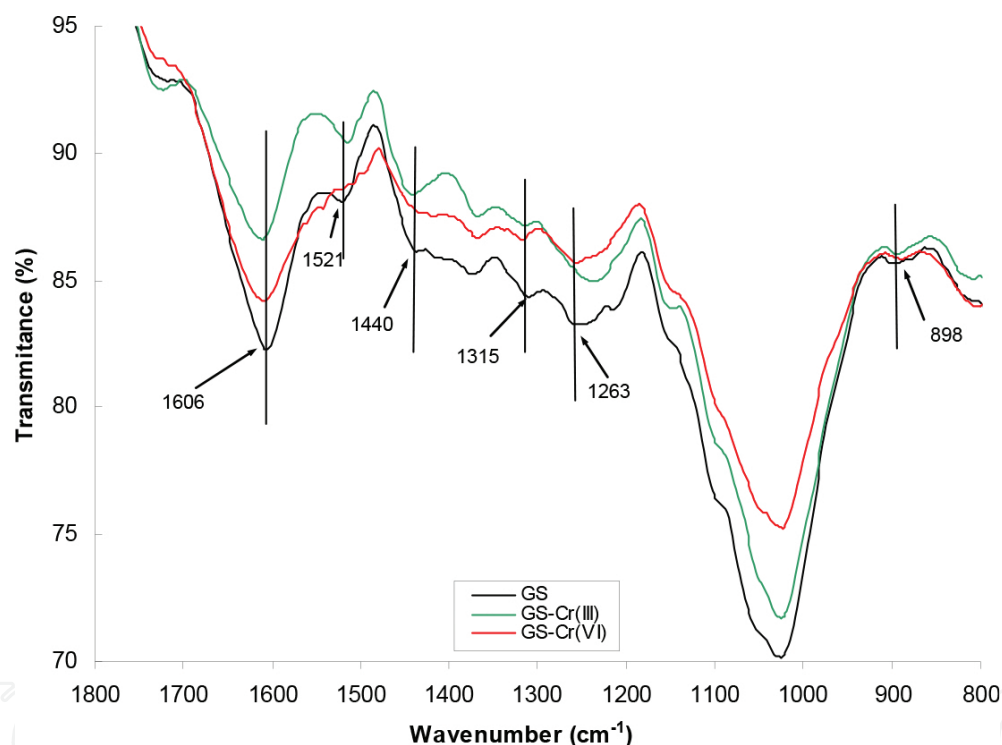
Figure 2. Grape stalks (GS) FTIR-ATR spectra before and after treatment with Cr(III) and Cr(VI) solutions. Initial metal concentration: 800 mg·L^{-1}. Agitation time: 24 h, pH_0 = 3.

The initial and final positions of the modified bands have been summarised in **Table 1**, including the assignment of the band to the functional group/s involved in Cr(III) and Cr(VI) sorption.

Grape stalks treated with Cr(III) and Cr(VI) solutions show modifications in the characteristic bands of syringyl and guaiacyl moieties (1263 and 1315 cm^{-1}, respectively), the methoxy deformation (1440 cm^{-1}), the aromatic skeleton vibration (1521 cm^{-1}) and the aromatic ring vibration (1606 cm^{-1}). All these bands, characteristic of the lignin macromolecule, indicate that

both Cr(III) and Cr(VI) are adsorbed onto this component of the sorbent, making the cellulose almost unaltered during the sorption process. The important role of lignin in sorption of copper and nickel onto the cork had been previously noticed in results of ^{13}CP-MAS-NMR on the solid phase of the sorbent [25].

| Frequency (cm⁻¹)				
GS	GS-Cr(III)	GS-Cr(VI)	Assignment	Ref.
898	897	898	Carbohydrates (unaltered)	[23]
1263	1238	1247	Guayacyl/C–O phenolic	[24]
1315	1319	1321	Syringyl	[23]
1440	1444	1421	Methoxy deformation	[23]
1521	1515	1511	Aromatic skeleton vibration	[23]
1606	1614	1612	C=C Aromatic vibration	[23]

Table 1. Observed frequencies and assignment.

3.2. Scanning electron microscopy-energy dispersive X-ray analysis

Scanning electron microscopy (SEM) coupled to energy dispersive X-ray analysis (EDX) is a powerful instrumental combination to assess the mechanisms governing heavy metal removal by lignocellulosic biomass. SEM provides a great magnification of the surfaces and allows gathering high-quality images, from which the morphology and topography of the materials can be assessed. The additional use of detection of backscattered electrons (BSE) helps finding target regions where metals may have been selectively accumulated in lignocellulosic biomaterials. EDX is widely used coupled to SEM and allows obtaining local elemental analysis of the surfaces under the observation. The technique becomes especially relevant in the assessment of sorption processes where local microprecipitation is likely to occur.

Metal microprecipitation takes place when the solubility of the sorbate reaches its limit. Microprecipitation in metal-removal processes—despite not being directly related to sorption—positively contributes to the overall detoxification of the effluent, since the metal microprecipitate remains immobilised in the surface and remains separated from the solution.
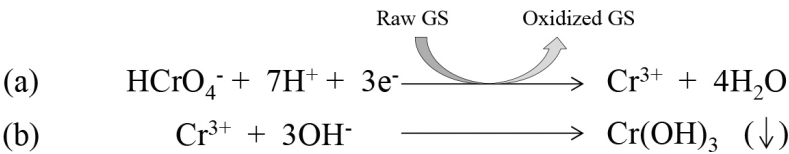
This may occur even due to local conditions, e.g. on or inside the sorbent, and not necessarily in the bulk of the solution. These favourable conditions for microprecipitation may be created by local deviations in physical conditions such as pH or by the presence of materials released from the sorbent itself. Escudero et al. [26] using SEM-BSE-EDX techniques observed microprecipitation phenomena when exploring the removal of hexavalent chromium by grape stalk wastes (GS) entrapped into calcium alginate gel beads. Micrographs in the SEM mode (a, d), BSE mode (b) and characteristic EDX spectra (c) are presented in **Figure 3**.
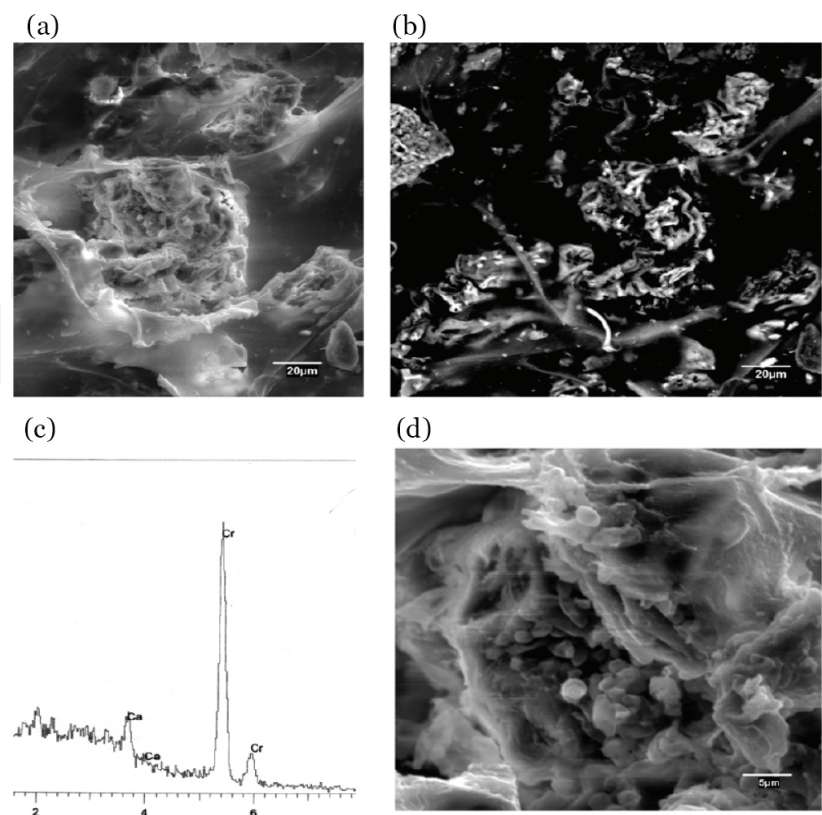
Figure 3. Electronic micrograph of grape stalks entrapped into a calcium alginate gel matrix exposed to a Cr(VI) solution. (a) Scanning mode, (b) backscattered electrons mode, (c) EDX local analysis and (d) focus on the grape stalk region in the SEM mode [26].

The observations indicated that chromium is mostly accumulated in the grape stalk surface, as it may be evidenced by the bright colour observed in the BSE picture (b). While magnifying the region, small nodules appear onto the surface of the grape stalks, indicating the formation of microprecipitates (d). The evidence of chromium accumulation in these nodules was further demonstrated through the EDX local analysis (c). Using further electron spin resonance analysis of the solids, the authors evidenced the formation of Cr(III). It was hypothesised then that Cr(VI) undergoes a reduction process that partially converts hexavalent into trivalent chromium with an associated large proton consumption (**Scheme 1a**). In this local alkalinised environment, Cr(III) precipitates onto the surface of the lignocellulosic material as hydroxide through reaction 1 (b) and remains isolated by the bulk of the solution by the surrounding calcium alginate gel.

$$\text{(a)} \qquad HCrO_4^- + 7H^+ + 3e^- \xrightarrow[\text{Raw GS} \quad \text{Oxidized GS}]{} Cr^{3+} + 4H_2O$$

$$\text{(b)} \qquad Cr^{3+} + 3OH^- \longrightarrow Cr(OH)_3 \ (\downarrow)$$

Scheme 1. Hexavalent chromium removal through a combined reduction-precipitation process promoted by grape stalks [26].

4. Immobilisation techniques: the use of hydrogels as high-permeable immobilising materials

Native biomass shows low density and poor mechanical strength and rigidity [27]. These properties make its application difficult in biosorption processes either in batch or in column. In the batch mode, mechanical stirring and shear forces can break fragile particles of the biosorbent resulting in particle attrition (breakage, fragmentation, fines formation) and then, a continuous change on the original particle size distribution. Particle size is a key parameter in the performance of sorption processes; it is desirable that size distribution remains homogeneous throughout the entire process. It is known that, to maximise mass transfer and sorption efficiency, the sorbent particle size of the sorbent must be as small as possible (maximising surface-to-mass ratio). Limitations in the use of small particle sizes are (i) sorbent should be easily handled and (ii) clogging in filters, columns, valves and pipes must be prevented.

In the case of continuous bed up-flow sorption processes (columns), additional problems due to the native biomass physical properties must be considered. Biomass needs to be wetted to allow free swelling of the particles prior to column filling and to remove the finest particles by natural flotation. In addition to this, the non-uniform shape of the native biomass hinders the estimation of a form factor (sphere, cylinder, ellipsoid) of the particles. This parameter is needed when formulating a model to describe sorption processes. Most of the aforementioned drawbacks and limitations can be overcome, however, by immobilisation of the biomass in a water-permeable polymeric matrix. Immobilisation of biomass provides several advantages over native biomass: (i) increase of mechanical resistance, (ii) increase of density, (iii) possibility of enhancement of effective surface area due to the use of biomass powder, (iv) easy handling and (v) achievement of precision in form factor, since immobilisation can yield quasi-spherical beads or granules.

Biomass immobilisation consists of the attachment or entrapment of biomass on a support. Immobilisation can be carried out by four different techniques: adsorption, covalent binding, entrapment and membrane confinement. Entrapment in a gel matrix or gel encapsulation is among the most widely studied methods for immobilisation of enzymes, microbial biomass and animal and plant cells, being calcium alginate one of the regularly used matrixes [28]. The support selection is of crucial importance and must be chosen according to the target application of the immobilised material. Applications of immobilisation techniques are found in different scopes of several fields such as biotechnology and pharmaceutical, environment, food and biosensor industries [29].

For the treatment of wastewater, support materials need to meet (among others) the following criteria: insoluble, non-biodegradable, non-toxic, high mechanical and chemical stability, high diffusivity and ease of immobilisation procedure [30]. Natural polymer derivatives of algal polysaccharides (alginate, carrageenan, agar and agarose) and chitosan (an amino polysaccharide derived from chitin) have been experimentally used. Crini [31] has recently reviewed the most important features of polysaccharide-based materials used as adsorbents.

One of the most used immobilisation supports is alginate [32]. Alginate is a common term used for natural polymers composed of linear, unbranched chains of varying lengths, proportions and sequences of 1,4 linked residues of β-D-mannuronic acid and α-L-guluronic acid residues [33]. As the composition of alginates depends on the source from which they are extracted, they can exhibit different physical and chemical properties. The main source of alginates are different species of brown seaweeds *Laminaria digitata* [34] and *Macrocystis pyrifera* [35]. One of the properties of alginates is that they can cross-link with divalent metal ions such as calcium, barium, copper, zinc and lead [36, 37] to form M^{2+}-alginate hydrogels. Alginate gelation takes place when divalent metals interact with blocks of acid residues resulting in the formation of a 3D network, which is usually described by an 'egg-box' model [38]. Calcium alginate is one of the most utilised entrapment matrixes in environmental studies. Heavy metals adsorption takes place via ion exchange between Ca^{2+} ions from the hydrogel and metal ions. Pandey et al. [39] studied Cr(VI, Pb(II) and Cu(II) by using calcium alginate beads and Jodra and Mijangos [40] determined the ion exchange selectivity of calcium alginate gels for heavy metals and found the selectivity order: Pb > Cu > Cd > Ni > Zn > Co. During the last years different types of biomass used for heavy metals sorption have been entrapped in calcium alginate with the aim of enhancing their sorption performance. Studies on fungi [41, 42], algae [43, 44], bacteria [45] and yeast [46] encapsulated in calcium alginate have been recently carried out. Nevertheless, studies on metal sorption by using vegetable wastes and specifically lignocellulosic materials encapsulated in calcium alginate are scarce. The most probable reason is the high capacity of calcium alginate itself to sorb heavy metal ions. The only example of vegetable waste can be found in the work of Ansari et al. [47]. The authors encapsulated rose waste biomass in calcium alginate beads to sorb Pb(II) and found that the immobilised biomass yielded to higher metal ion sorption. Unfortunately, the authors did not report the amount of lead sorbed by pure calcium alginate beads.

Grape stalks, a lignocellulosic waste produced in wine production, was entrapped in calcium alginate and used for Cr(VI) removal at pH 3 in batch mode [48–50] and in column [51] from single metal solutions and from binary mixtures containing Cr(VI) and Cr(III) [52]. A scheme of a typical arrangement to obtain gel beads by the dropping technique is presented in **Figure 4**.
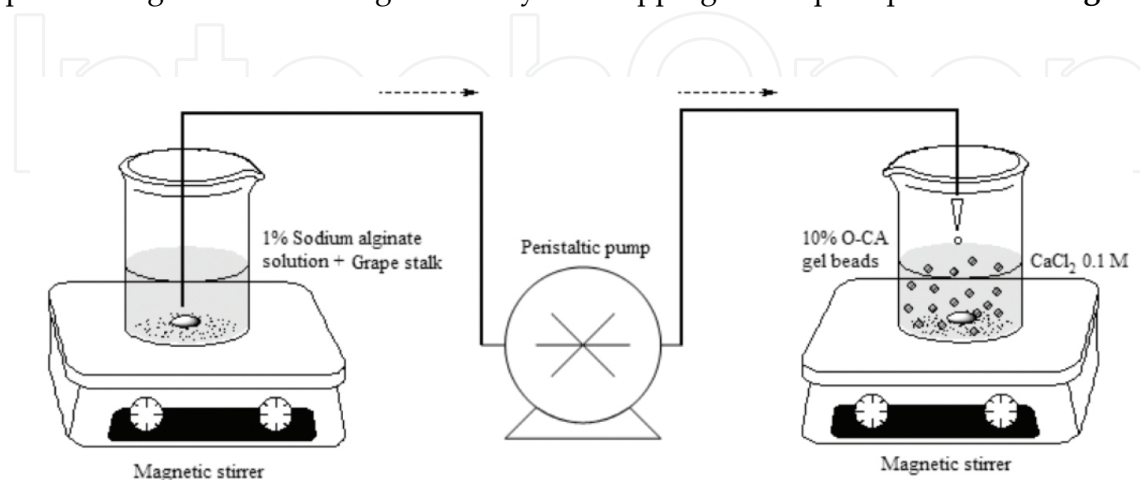
Figure 4. Entrapment procedure to obtain gel beads of grape stalks using calcium alginate [48].

Grape stalks were reported to be a very effective reducing agent to reduce Cr(VI) to Cr(III) [53]. Results of the above-mentioned studies with grape stalk demonstrated that both sorption and reduction processes were enhanced when the sorbent was immobilised into calcium alginate. Furthermore, the Cr(III) formed as a consequence of the reduction reaction was sorbed onto calcium alginate beads via ion exchange with calcium ions. It must be remarked that at pH 3 major chemical species of Cr(VI) is $HCrO_4^-$ that is hardly sorbed by calcium alginate beads. Therefore, the joint action of both sorbents under appropriate conditions can lead to the total elimination of Cr(VI) [26].

Treatment phase			
Electrochemical treatment		**Biosorption-based treatment**	
1. Electrochemical reduction	**Subtotal**	**1. Batch reactor**	**Subtotal**
Electricity	1.560	Stirring	780
2. Reagent addition	**Subtotal**	**2. Biosorbent addition**	**Subtotal**
Sodium hydroxide (NaOH)	500	Sodium hydroxide (NaOH)	500
Hydrochloric acid (HCl)	100	Hydrochloric acid (HCl)	100
Coagulant	2000	Grape stalks	21
3. Control sensors and separation unit	**Subtotal**	**3. Control sensors and separation unit**	**Subtotal**
Electrodes (pH and redox)	1000	Electrodes (pH and redox)	1000
Filter clothes	100	Filter clothes	100
Energy	200	Energy	200
4. Waste management	**Subtotal**	**4. Waste management**	**Subtotal**
Waste collection	240	Waste collection	240
post-treatment phase			
Electrochemical treatment		**Biosorption-based treatment**	
5. Treatment with activated carbon	**Subtotal**	**5. Treatment with biosorbent**	**Subtotal**
Activated carbon	134.4	Grape stalks	1.2
		Sodium alginate	339.4
Other expenses			
Electrochemical treatment		**Biosorption-based treatment**	
Internal labour costs	3000	Internal labour costs	1500
External labour costs	1000	External labour costs	750
Pumps and valves	1000	Pumps and valves	1000
Total	**10,834€**	**Total**	**6532€**

Table 2. Comparison between electrolytic and biosorption-based schemes for the treatment of 300 m³/year of wastewater from an electroplating water industry. Costs are expressed in €.

The authors of the present chapter carried out a thorough techno-economical study concerning implementation of biosorption-based technology for the treatment of wastewater from an electroplating industry (unpublished data). A brief economic summary showing the different technological processes involved and their related expenses is presented in **Table 2**. The table compares the costs related to the use of regular technology (based on electroreduction) with the ones associated with a water treatment based on biosorption/bioreduction by grape stalks (GS) and precipitation/refining using GS entrapped into calcium alginate (CA).

In a regular wastewater treatment, Cr(VI) is reduced to Cr(III) using electricity. In acidic media, 3 mols of electrons are consumed in this process per mol of Cr(VI) reduced. In the case of the GS sorption/reduction process, there is no electric current applied to the solution and the only energetic requirements are related to the mixing of the material with the Cr(VI) solution. Avoiding electrochemical reduction in the treatment phase, decreases the costs related to energy consumption to half (from 1560 to 780€). In terms of reagents, NaOH and HCl are reagents used in both treatment schemes. In the secondary phase (post-treatment or refining), the costs related to the use of activated carbon are about 134€. Using GS and CA for the removal of residual Cr(VI) and the formed Cr(III) involve about 341€. In terms of other expenses, there is both an internal and external labour costs reduction when biosorption-based technologies are used. This saving is due to the frequent cleaning and, in the last term, replacement of the electrodes in the electrochemical cells. In the case of a biosorption unit, repairs are less frequent and maintenance less expensive.

Overall, the use of GS and CA in the detoxification of Cr(VI) polluted effluents involves a saving close to 40% if compared to the electrochemical reduction process. These data are just an example that clearly shows the viability of lignocellulosic materials for real wastewater treatment. There is a clear opportunity to go beyond the laboratory studies and implement properly scaled biosorption processes to the treatment of real industrial effluents.

5. Equilibrium and kinetics modelling

5.1. Equilibrium models in single component solutions

A precise mathematical description of the equilibrium isotherms is of paramount importance for the effective design of sorption systems. The most widely used adsorption isotherms found in the literature to describe the amount of solute adsorbed as a function of the equilibrium concentration in solution are summarised in **Table 3**.

From these models, by far the most widely employed are Langmuir and Freundlich. While Langmuir isotherm model relies on the adsorption theory and assumes the formation of a sorbate monolayer, Freundlich isotherm is an empirical model to correlate the concentration of a sorbate on the solid phase and the concentration of the sorbate in the fluid.

Isotherm model	Equation	Linear expression	Ref.
Langmuir	$q_e = \dfrac{Q_m b C_e}{1 + b C_e}$	$\dfrac{C_e}{q_e} = \dfrac{1}{b Q_m} + \dfrac{C_e}{Q_m}$	[54–56]
Freundlich	$q_e = k_F C_e^{\frac{1}{n_F}}$	$\ln q_e = \ln k_F + \dfrac{1}{n}\ln C_e$	[54–56]
Redlich-Peterson	$q_e = \dfrac{K_{RP} C_e}{1 + \alpha_{RP} C_e^{\beta}}$	$\ln\left(\dfrac{K_{RP} C_e}{q_e} - 1\right) = \ln \alpha_{RP} + \beta \ln C_e$	[55, 56]
Sips	$q_e = \dfrac{Q_m b C_e^{n_S}}{1 + b C_e^{n_S}}$		[54–56]
Temkin	$q_e = \dfrac{RT}{b_T}\ln(K_T C_e)$	$q_e = \dfrac{RT}{b_T}\ln K_T + \dfrac{RT}{b_T}\ln C_e$	[54–56]
Dubinin-Radushkevich	$q_e = Q_m \exp\left(-B_D \varepsilon^2\right)$ $\varepsilon = RT\ln\left(1 + \dfrac{1}{C_e}\right)$	$\ln q_e = \ln Q_m - 2 B_D R^2 T^2 \ln\left(1 + \dfrac{1}{C_e}\right)$	[55, 56]
Toth	$q_e = \dfrac{Q_m b C_e}{\left(1 + \left(b C_e\right)^t\right)^{\frac{1}{t}}}$		[54, 56]

Table 3. Mathematical equations of single component isotherm models.

Obtaining isotherm parameters from experimental data is a key aspect to consider. Using linear regression to determine the sorption isotherm parameters and decide which model provides the best fit was not only the easiest way at the time this approach was proposed, but also has become a 'custom' extended to our days. Obviously, the linearisation of the equations involves a transformation of the data in a process that alters the structure of errors, violates the error variance assumptions and the normality of the least squares method [57–59]. This set of error sources explains that the linear parameters obtained through Freundlich model produces isotherms that best fit data at low concentrations, while the linear parameters of the Langmuir tend to better match isotherm data at higher concentrations [57, 60]. Taking into account the aforementioned drawbacks of the linear procedures, direct calculation of the isotherm parameters through non-linear optimisation methods is strongly recommended. The non-linear optimisation is a more complex method than the linearisation approach and requires the proper choice of an error function to accurately evaluate the fit of the experimental results

to the chosen isotherm, since the choice of the error function may affect the derived parameters. The most widely used error functions to fit sorption isotherm data are summarised in **Table 4**.

Error function	Expression	Ref.
The sum of the squares of the errors (SSR)	$$\sum_{i=1}^{N} \left(q_{i,\exp} - q_{i,cal}\right)^2$$	[54, 57, 61]
Hybrid fractional error function (HYBRD)	$$\frac{100}{N-p} \sum_{i=1}^{N} \frac{\left(q_{i,\exp} - q_{i,cal}\right)^2}{q_{i,\exp}}$$	[54, 57, 61]
Marquardt's percent standard deviation (MPSD)	$$100\sqrt{\frac{1}{N-p} \sum_{i=1}^{N} \left(\frac{q_{i,\exp} - q_{i,cal}}{q_{i,\exp}}\right)^2}$$	[54, 57, 61]
Average relative error (ARE)	$$\frac{100}{N} \sum_{i=1}^{N} \left| \frac{q_{i,\exp} - q_{i,cal}}{q_{i,\exp}} \right|$$	[54, 57, 61]
Sum of the absolute errors (EABS)	$$\sum_{i=1}^{N} \left| q_{i,\exp} - q_{i,cal} \right|$$	[54, 57, 61]

Table 4. Error functions.

The sum of the squares of the errors (SSR) is the most widely used error function, but it shows an important drawback; the isotherm parameters obtained provides a better fit in the case of high concentrations due to the fact that errors and therefore their squares increase, when it does the concentration.

Hybrid fractional error function (HYBRD) is an error function developed with the attempt of improving the adjustment of the SSR at low concentrations divided by the measured value and includes the degrees of freedom of the system.

Marquardt's percent standard deviation (MPSD) is similar in some aspect to a geometric mean error distribution modified according to the number of degrees of freedom of the system.

Average relative error function (ARE) attempts to minimise the fractional error distribution across the entire concentration range.

Sum of the absolute errors (EABS) uses a similar approach to that used in the SSR. Isotherm parameters determined using this error function provide a better fit as the magnitude of the error increases, biasing the fit towards the high concentration data [61].

In terms of least-squares regression analysis, one of the central premises is that the independent variable x remains fixed, i.e. there is no measured error in x. Therefore, there should be no error in the measurement of the equilibrium concentration in solution (C_e). However, the

determination of the remaining concentration in the solution is not free from error, despite careful calibration and repetition of sample analysis is performed. Hence, the application of orthogonal distance regression (ODR) may be appropriate [59, 62–65].

The ODR takes into account the errors in both variables (C_e and q). The most widely used error functions are summarised in **Table 5**.

Error function	Expression	Ref.
Theoretical orthogonal distance regression	$$\sum_{i=1}^{N}\left[\left(\frac{q_{i,\exp}-q_{i,cal}}{\sigma_{\varepsilon i}}\right)^2+\left(\frac{C_{ei,\exp}-C_{ei,cal}}{\sigma_{\delta i}^e}\right)^2\right]$$	[59, 63]
Orthogonal distance regression	$$\sum_{i=1}^{N}\left[\left(\frac{q_{i,\exp}-q_{i,cal}}{q_{i,\exp}}\right)^2+\left(\frac{C_{ei,\exp}-C_{ei,cal}}{C_{ei,\exp}}\right)^2\right]$$	[62, 63, 65, 66]
Experimental weighted orthogonal distance regression	$$\sum_{i=1}^{N}\left[\left(\frac{q_{i,\exp}-q_{i,cal}}{sdy_i}\right)^2+\left(\frac{C_{ei,\exp}-C_{ei,cal}}{sdx_i}\right)^2\right]$$	[63]
Triplicate orthogonal distance regression	$$\sum_{i=1}^{N}\left[\left(\frac{q_{i,\exp}-q_{i,cal}}{q_{i,\exp}}\right)^2+\left(\frac{C_{ei,\exp}-C_{ei,cal}}{C_{ei,\exp}}\right)^2\right]$$	[63]

Table 5. Error functions.

5.2. Equilibrium models in multicomponent solutions

Since the interaction of a component with other components in a mixture can be synergistic, antagonistic or non-interactive, the biosorption results cannot be predicted on the basis of studies derived from single component solutions. The behaviour of each species in a multi-component system depends largely on the physical and chemical properties of both, sorbent and sorbate. However, most of the isotherms of a single component can be extended to describe a multi-component adsorption system. The most frequently used extensions are summarised in **Table 6**.

In the scientific literature, there are few models to describe synergistic effects in sorption processes. A straightforward and simple way to develop a synergistic model is based on the use of monocomponent models and introduction of correction factors, for example, by combining a single isotherm (Langmuir, Freundlich, etc.) with a form factor $1+F_i(C)$ [72, 73].

When it comes to obtaining the parameters of these models, the same comments stated previously for monocomponent sorption isotherms applies. The error function most widely used is based on the sum of the SSR for each component although the most suitable method would be the use of ODR.

Isotherm model	Equation	Ref.
Extended Langmuir:	$$q_{e,i} = \frac{q_{0,i} b_i C_{e,i}}{1 + \sum_j b_j C_{e,j}}$$	[67–69]
Modified competitive Langmuir:	$$q_{e,i} = \frac{q_{0,i} b_i \dfrac{C_{e,i}}{\eta_i}}{1 + \sum_j b_j \dfrac{C_{e,j}}{\eta_j}}$$	[67, 70, 71]
Extended Freundlich:	$$q_{e,i} = \frac{K_{F,i} C_{e,i}^{\frac{1}{n_i} + x_i}}{C_{e,i}^{x_i} + y_i C_{e,j}^{z_j}}$$	[67, 68]
Competitive non modified Redlich Peterson model:	$$q_{e,i} = \frac{K_{RP,i} C_{e,i}}{1 + \sum_j a_{RP,j} C_{e,j}^{\beta_j}}$$	[67, 68]
Competitive modified Redlich Peterson model:	$$q_{e,i} = \frac{K_{RP,i} \dfrac{C_{e,i}}{\eta_i}}{1 + \sum_j a_{RP,j} \left(\dfrac{C_{e,j}}{\eta_j}\right)^{\beta_j}}$$	[68]

Table 6. Multicomponent equilibrium models.

5.3. Kinetics models

A summary on the most widely used models to describe the time-course profile of metal removal in sorption processes is presented in **Table 7**.

The scientific literature to date shows that, in most cases, the obtention of the characteristic parameters of the aforementioned models is performed through linearisation. As previously discussed, this process involves a transformation of the data set and the subsequent alteration of the error structure and therefore a given bias in the so obtained parameters. To avoid this, non-linear regression should be used using the SSR as target error function. In this case, the use of ODR is not strictly needed since it can be considered that there is no error in the accurate determination of the time variable.

As a final remark, it should be highlighted that a good fitting of an experimental data set to a given kinetic or equilibrium model does not necessarily imply that the sorption process is governed by the mechanisms on which the model relies [74].

Kinetic model	Equation	Linear expression	Ref.
Pseudo-first-order or Lagergren equation	$\frac{dq_t}{dt} = K_1(q_e - q_t)$ $q_t = q_e(1 - \exp(-K_1 t))$	$\ln(q_e - q_t) = \ln q_e - K_1 t$	[56, 74]
Pseudo-second-order	$\frac{dq_t}{dt} = K_2(q_e - q_t)^2$ $q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}$	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$	[56, 74]
Weber-Morris or intra-particle diffusion	$q_t = K_P t^{\frac{1}{2}}$		[56, 74]
Elovich equation	$\frac{dq_t}{dt} = a_E \exp(-\alpha_E q_t)$ $q_t = \frac{1}{\alpha_E}\ln(t + t_0) - \frac{1}{\alpha_E}\ln(t_0)$ $t_0 = \frac{1}{a_E \alpha_E}$		[74]

Table 7. Kinetic models.

6. Metal desorption and regeneration of lignocellulosic wastes

Metal laden biomass can either be directly disposed or incinerated, delivering the ashes to a regular hazardous waste landfill. Incineration reduces waste volume, but enhances the metal content per mass unit and may cause environmental issues due to potential toxic metal leaching. Disposal or incineration of metal-laden biomass is recommended when biomass is abundant and cheap and metal is not worth recovering. Another alternative is regeneration of the biomass by elution of the loaded metal using desorbing agents. The selection criteria that guides to choose the appropriate desorbing agent are: (i) small volume of eluent should yield high metal concentration in the resulting solution, (ii) the structural integrity of the biomass must not be severely affected, and (iii) the eluent should be economic and environmentally friendly.

Most of the desorbing agents used for sorbents regeneration and metal recovery are based on strong mineral acids (HCl, HNO₃, H₂SO₄), short-chain organic acids (HCOOH, CH₃COOH), bases (NaOH, NaHCO₃, Na₂CO₃, KOH, K₂CO₃), salts (NaCl, KCl, CaCl₂, KNO₃), chelating agents (ethylenediaminetetraacetic (EDTA), diethylenediaminepentacetic (DTPA), nitrilotri-acetic (NTA)) or buffer solutions (phosphate, bicarbonate). Recently, the most widely used desorbing agents have been reviewed [75].

The most used desorption agents to remove metal-laden lignocellulosic biomass are acids. An acidic solution (pH 2.0) was found to be the best desorbing solution for Cu(II) and Cr(VI) loaded onto commercial coffee wastes [76]. A 0.1 M HCl solution resulted to be effective to desorb Cd(II) (83.9%) from rice husk in both batch and column modes [77]; Cu(II) (99.4%), Cd(II) (98.5%) and Zn(II) (99.3%) from papaya wood [78]; As(V) from coconut coir pith [79]; Cu(II) from cork and yohimbe bark [80]; and 0.2 and 0.5 M HCl for chromium recovery from avena by-products and Ga(III) desorption from coir [71]. A 0.1 M HNO_3 solution was used by Gupta and Nayak [81] to desorb 98.2% Cd(II) loaded onto orange peel powder with Fe_3O_4. Higher concentrations than 0.01 M of HNO_3 and HCl were needed to effectively desorb Cd(II) loaded onto coffee beans [82]. *Ficus religiosa* lead(II) laden was regenerated by using 0.05 M HNO_3 [83]. HCl and EDTA solutions were used to desorb U(VI) from citrus waste material. The best desorption yields were obtained by 0.1 EDTA (94.7%) followed by 0.1 HCl (89.71%) [84]. HCl and EDTA were also tested by Martinez et al. to recover Pb, Cu, Cd and Ni from grape stalk and olive stones wastes, the former being the most effective [85, 86].

Alkaline solutions were also successfully tested as desorbing agents for metal ions from biomass. Note that 0.5 M sodium citrate was able to remove lead(II) laden on hop by-products [87]. Elution of arsenic-laden rice polish and rice husk packed columns was achieved by passing through the column of 10% NaOH [88] and 1 M KOH [89] solutions, respectively.

The main conclusion retrieved from the literature survey is that recovery of metals from exhausted lignocellulosic materials and other low-cost sorbent materials and the regeneration of the sorbent is not nowadays the focus of researchers. It may be foreseen however that in the future, when some metals become scarce, further research will be conducted to find out selective metal desorbing agents that meet the most of the aforementioned criteria.

7. Conclusion

Lignocellulosic biomass has a huge potential as a low cost, renewable source and environmentally friendly alternative to conventional methods for the removal of heavy metals from aqueous polluted streams. This technology is of special interest to treat large volumes of effluent containing low metal concentration to produce a final effluent that does not pose environmental hazards. A thorough screening and selection of the most effective low-cost sorbents with sufficiently high metal-binding capacity and selectivity for heavy metal ions are prerequisites for full-scale implementation in industrial processes. Despite further research, efforts towards full understanding of sorption mechanisms and development of more accurate mathematical models might be required, the technology can be considered mature enough as to face scale-up scenarios to large scale. Industrial stakeholders, policymakers and regulators have nowadays a challenging and exciting opportunity to take a step forward towards environmental sustainability considering sorption onto biomaterials on their wastewater treatment schemes.

Annex 1: Notation

q_e	Amount of sorbate adsorbed per unit mass of sorbent at equilibrium
Q_m	Maximum uptake of sorbate per unit mass of sorbent
b	Langmuir constant related to sorbent affinity
C_e	Concentration of sorbate in solution at equilibrium
k_F	Freundlich constant related to the amount of sorbate adsorbed
n_F	Freundlich constant related to sorption intensity
K_{RP}	Redlich-Peterson constant related to the amount of sorbate adsorbed
α_{RP}	Redlich-Peterson constant
β	Redlich-Peterson exponent $0 \leq \beta \leq 1$
n_S	Sips constant related to sorption intensity
R	Universal gas constant
T	Temperature
b_T	Temkin constant
K_T	Temkin constant related to binding
B_D	Dubinin-Radushkevich constant related to sorption energy
ε	Polanyi potential
τ	Toth model exponent
$q_{i,exp}$	Experimental data values
$q_{i,cal}$	Data values calculated from the model
N	Number of data
p	Number of model parameters
$\sigma_{\varepsilon i}$	Population standard deviation of measurement error in dependent variable
$\sigma_{\delta i}^{e}$	Population standard deviation of measurement error in equilibrium concentration
sdy_i	Estimates of population standard deviation for dependent variable
sdx_i	Estimates of population standard deviation for independent variable
η	Dimensionless interaction factor
q_t	Amount of sorbate adsorbed per unit mass of sorbent at time t
K_1	First-order reaction rate equilibrium constant
K_2	Second-order reaction rate equilibrium constant
t	Time
K_p	Intra-particle diffusion rate constant
a_E	Elovich equation constant
α_E	Elovich equation constant

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