



HAL
open science

Conventional and non-conventional adsorbents for wastewater treatment

Grégorio Crini, Eric Lichtfouse, Lee Wilson, Nadia Morin-Crini

► **To cite this version:**

Grégorio Crini, Eric Lichtfouse, Lee Wilson, Nadia Morin-Crini. Conventional and non-conventional adsorbents for wastewater treatment. *Environmental Chemistry Letters*, 2019, 17 (1), pp.195-213. 10.1007/s10311-018-0786-8 . hal-02082916

HAL Id: hal-02082916

<https://hal.science/hal-02082916v1>

Submitted on 28 Mar 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Conventional and non-conventional adsorbents for wastewater treatment

Grégoire Crini¹ · Eric Lichtfouse² · Lee D. Wilson³ · Nadia Morin-Crini¹

Abstract

The removal of contaminants from wastewaters is a major challenge in the field of water pollution. Among numerous techniques available for contaminant removal, adsorption using solid materials, named adsorbents, is a simple, useful and effective process. The adsorbent matter can be mineral, organic or biological. Activated carbon is the preferred, conventional material at the industrial scale. Activated carbon is extensively used not only for removing pollutants from wastewater streams, but also for adsorbing contaminants from drinking water sources, e.g., groundwater, rivers, lakes and reservoirs. However, the widespread use of activated carbon is restricted due to a high cost. In the last three decades, numerous approaches using non-conventional adsorbents have been studied for the development of cheaper and more effective adsorbents to eliminate pollutants at trace levels. This review gives an overview of liquid–solid adsorption processes using conventional and non-conventional adsorbents for pollutant removal. The manuscript outlines the principles of adsorption and proposes a classification for adsorbent materials. Finally, the various mechanisms involved in the adsorption phenomena are discussed.

Keywords Wastewater treatment · Pollutants · Adsorption · Commercial adsorbents · Non-conventional adsorbents · Green adsorbents · Mechanism

Introduction

Man's use of chemical substances, in particular metals, began to affect the environment during the “*Industrial Revolution*.” Although some metal ions are disseminated into the environment naturally by both geological and biological activity, human activity today produces a greater input. The

toxicity of many of these pollutants/contaminants is well known. Today, we are in the “*Pollutant Removal Age*” and, it is, therefore, not surprising that there has been considerable effort to develop technologies to reduce contaminant emissions (Morin-Crini and Crini 2017). A significant proportion of these emissions are in the form of industrial wastewaters. Indeed, the industrial sector consumes significant volumes of water and consequently generates considerable amounts of wastewater discharge containing both mineral and organic contamination. This sector is today considered to be one of the most polluting in spite of the considerable effort made to clean up the processes over the last 30 years (Landy et al. 2012a, b; Khalaf 2016; Morin-Crini and Crini 2017).

Wastewater treatment is becoming ever more critical due to diminishing water resources, increasing wastewater disposal costs, and stricter discharge regulations that have lowered permissible contaminant levels in waste streams. The diversity of water pollutants calls for a wide range of treatment methods that are not only effective, but also technologically and economically feasible. The most common methods for the removal of contaminants from industrial effluents include biodegradation, precipitation, chemical oxidation, solvent extraction, evaporation, electrochemical

✉ Grégoire Crini
gregorio.crimi@univ-fcomte.fr

Eric Lichtfouse
eric.lichtfouse@inra.fr

Lee D. Wilson
lee.wilson@usask.ca

Nadia Morin-Crini
nadia.crimi@univ-fcomte.fr

¹ Laboratoire Chrono-environnement, UMR 6249, UFR Sciences et Techniques, Université Bourgogne Franche-Comté, 16 Route de Gray, 25000 Besançon, France

² CNRS, IRD INRA, Coll France, CEREGE, Aix Marseille University, Aix-en-Provence, France

³ Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, SK S7N 5C9, Canada

approaches, cementation, membrane filtration, phytoremediation, ion-exchange and carbon adsorption (Volesky 1990; Harvey et al. 2002; Crini and Badot 2007; Cox et al. 2007; Sharma 2015; Morin-Crini and Crini 2017).

Over the last few decades, adsorption has gained importance as a separation, purification and/or detoxification process on an industrial scale. Adsorption is used to purify, decolorize, detoxify, deodorize, separate and concentrate to allow removal and to recover the harmful products from liquid solutions and gas mixtures (Dąbrowski 2001; Crini and Badot 2010; Kyzas and Kostoglou 2014). Adsorption is—along with biodegradation—one of the two major treatments applied to the decontamination of water due to its convenience, easy operation and simplicity of design, high efficiency and also for its wider applicability in water pollution control (McKay 1996; Babel and Kurniawan 2003; Swami and Bud-dhi 2006; Crini 2006; Qu 2008; Vijayaraghavan and Yun 2008; Gadd 2009). From an industrial point of view, adsorption is both technologically simple and economically feasible while also being a process that produces high-quality water, with pollutant concentrations under the legal limits for discharge waters. In general terms, activated carbons must be thought of as being most effective adsorbents and, as such, their performance in removing contaminants such as metals, radionuclides, rare earth elements, dyes, phenolic and aromatic derivatives, pesticides, pharmaceuticals and drugs has been examined widely (Dąbrowski et al. 2005). Attention has also focused on adsorption onto commercial activated alumina, ion-exchange using organic polymeric resins and zeolites as other non-consumptive materials (Wang and Peng 2010). However, despite the excellence of their performance, these systems are expensive to use and, as such, cannot be thought of as a truly viable option in many parts of the world.

Because of this, attention has turned to the adsorptive properties of other non-conventional solid materials proposed as low-cost, efficient and green adsorbents for pollutant removal (Pollard et al. 1992; Ramakrishna and Viraraghavan 1997; Houghton and Quarmby 1999; Blackburn 2004; Gavrilescu 2004; Crini 2005, 2006; Li et al. 2008; Oliveira and Franca 2008; Ngah and Hanafiah 2008; Gupta and Suhas 2009; Rafatullah et al. 2010; Crini and Badot 2010). The past three decades have shown an explosion in the development of new materials including new carbons produced from wastes or natural by-products, natural or synthetic adsorbents or sorbents, and biological materials or biosorbents.

This review presents adsorption processes as a decontamination method for the removal of contaminants from synthetic solutions and industrial effluents. It outlines some of the principles of contamination adsorption onto solid materials. The review also proposes a classification for the different types of materials used and discusses different

mechanisms involved in the adsorption phenomena. This article is an abridged version of the chapter published by Crini et al. (2018) in the series Environmental Chemistry for a Sustainable World.

Wastewater treatment by adsorption

Definition

Adsorption is a process of separation during which the substances of a fluid, liquid or gas, bind to the exterior and interior surfaces of a solid material called the adsorbent. The separation is based on the selective adsorption, i.e., thermodynamic and/or kinetic selectivity, of the contaminants by an adsorbent owing to specific interactions between the surface of the adsorbent material and the adsorbed contaminants: simple mass transfer from the liquid phase toward the solid phase (Dubinin 1966). This surface phenomenon is a manifestation of complicated interactions among the three components involved, i.e., the adsorbent, the adsorbate and the wastewater, e.g., effluent, synthetic solution or water. Figure 1 shows a schematic adsorption model for the three components and their interactions. Generally, in this ternary system, the affinity between the adsorbent and the adsorbate is the main interaction force controlling adsorption (Furuya et al. 1997; Crini 2005; Crini and Badot 2010). However, the affinities between the adsorbate and the solution, the adsorbent and the solution, and the contaminant molecules can also play a major role in adsorption. In aqueous solution, hydrophobic compounds have low solubility and tend to be pushed to the adsorbent surface. It is reasonable to expect that adsorption capacity will be dependent upon the interaction forces between the three adsorption components.

Adsorption, sorption, biosorption, absorption or bioaccumulation: what is the most appropriate term?

“Adsorption,” “sorption,” “biosorption,” “bio-adsorption,” “absorption” or “bioaccumulation”: What is the

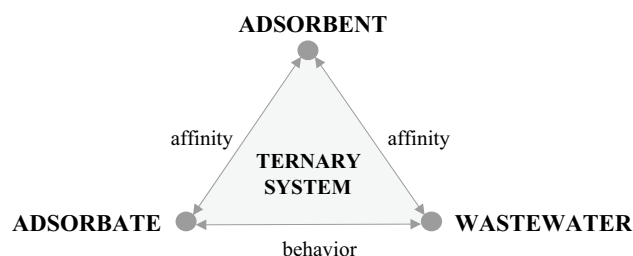


Fig. 1 Relationships between the three components of an adsorption system (Crini 2005)

most appropriate term? Although this is not difficult to answer, there is a lot of confusion in the abundant literature (Dąbrowski et al. 2005; Crini 2005, 2010; Gadd 2009).

The change in the concentration of a molecule in the surface layer of a solid material in comparison with the bulk phase with respect to unit surface area is termed adsorption. Sorption is a general term used for both absorption and adsorption (Crini 2010). These terms are often confused. Absorption is the incorporation of a substance in one state into another of a different state (e.g., liquids being absorbed by a solid or gases), i.e., into a three-dimensional matrix (Gadd 2009). Adsorption is the physical adherence or bonding of molecules (or ions) onto the surface of another substance, i.e., onto a two-dimensional surface. In this case, the material accumulated at the interface is the adsorbate and the solid surface is the adsorbent.

Adsorption, strictly speaking, defines binding in terms of a physical rather than chemical surface phenomenon. In processes using carbons, adsorption is generally the preferred term (Dąbrowski 2001; Dąbrowski et al. 2005). If adsorption occurs and results in the formation of a stable molecular phase at the interface, this can be described as a surface complex. Two general kinds of surface complex exist: inner- and outer-sphere surface complexes. An interesting discussion on this subject can be found in the review by Gadd (2009). Adsorption is the most common treatment used in conventional cleanup technologies, but unless it is clear which process, absorption or adsorption, is operative, sorption is a more general term, and can be used to describe any system where a sorbate, e.g. a molecular ion, a molecule, a polymer, interacts with a sorbent—i.e., a solid surface—resulting in an accumulation at the sorbate–sorbent interface.

Biosorption or bio-adsorption may be simply defined as the removal of substances from solution by biological materials (Gadd 1990; Garnham 1997; Volesky 2001; Veglio and Beolchini 1997; Davis et al. 2003; Vijayaraghavan and Balasubramanian 2015). This is a physicochemical process and includes several mechanisms. The precise binding mechanisms may range from physical, i.e., electrostatic interactions, van der Waals forces, hydrogen bond, to chemical binding, i.e., ionic and covalent. Some of the reported mechanisms include absorption, (surface) adsorption, ion-exchange, binding or surface complexation, (surface) precipitation or microprecipitation, and mineral nucleation. Biosorption is a property of both living and dead organisms, and their components. While most biosorption research concerns metals and related substances (Gadd 1990), the term is now applied to particulates and all manner of organic substances as well. Practically, all biological material has an affinity for metal species (Wase and Forster 1997; Aksu 2005; Gadd 2009). However, the term “biosorption” refers to passive or physicochemical attachment of a sorbate to a biosorbent, essentially the binding of a chemical species to

biopolymers. The definition, thus, specifically excludes metabolic or active uptake by living, metabolizing cells. In the literature, the term “biosorbent” includes the usage of dead biomass such as fibers, peat, rice hulls, forest by-products, chitosan and agro-food wastes as well as living plants, fungi, algae (unicellular microalgae, cyanobacteria, multicellular macroalgae) and bacteria. Biosorbents represent cheap filter materials often with high affinity, capacity and selectivity, and they are abundant and already available in most places (Aksu 2005; Sudha and Giri Dev 2007; Vijayaraghavan and Yun 2008; Gadd 2009; Crini and Badot 2010; Michalak et al. 2013; Kyzas et al. 2013; Lim and Aris 2014; Ong et al. 2014; Gupta et al. 2015). Some types of materials are broad range with no specific priority for metal ion bonding, while others can be specific for certain types of metal ions.

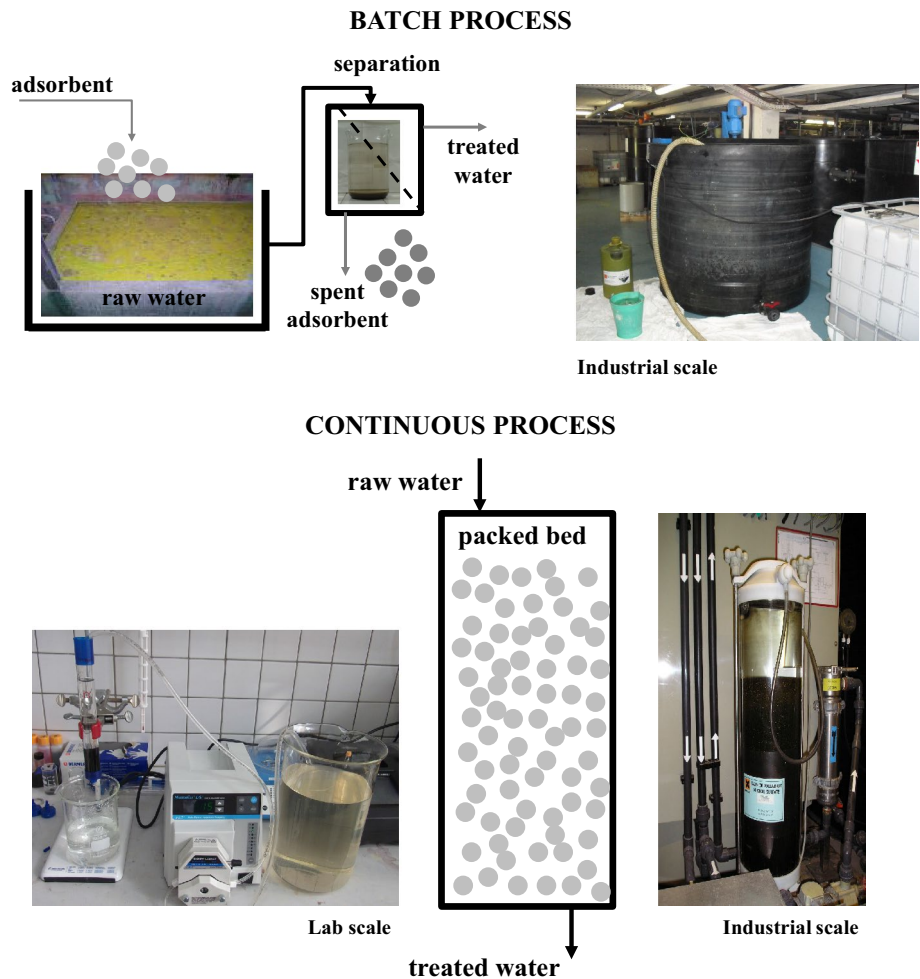
“Bioaccumulation” is also another term which induces confusion. Using biosorbents such as algae for metal ions removal, another mechanism can occur. Indeed, precipitation or crystallization of metals may occur within and around cell walls as well as the production by biomass of metal-binding polysaccharides: These processes which could be considered as biosorption are better termed “bioaccumulation” (Gadd 1990; Garnham 1997). These two terms “biosorption” and “bioaccumulation” have been adopted for the description of the two mechanistically different types of metal sequestering by microorganisms. The first has been proposed for the sequestration by non-metabolically mediated process (inactive microorganisms), and the second for the sequestration of metal ions by metabolically mediated processes (living microorganisms). Biosorption tends to be very rapid and reversible, while bioaccumulation tends to be slower and irreversible. An interesting discussion on the features of biosorption and bioaccumulation can be found in the review by Vijayaraghavan and Yun (2008). So, there are mechanistic differences between these two terms. However, the two mechanisms can coexist in a biosorption system and can also function independently.

Contacting systems

It is important to consider the modes of contacting the solid adsorbent and the wastewater when applying the adsorption system to both industrial large-scale treatments and laboratory scale (McKay 1996; Bajpai and Rajpoot 1999; Ali 2014). There are several types of contacting systems available to obtain experimental data and for industrial applications, including batch methods, fixed-bed-type processes, pulsed beds, moving mat filters and fluidized beds. However, the two most frequently used systems applied in solid/liquid adsorption processes are the batch-type contact and fixed-bed-type processes (Fig. 2).

Adsorption processes for decontamination of wastewaters can be carried out either discontinuously in batch reactors or

Fig. 2 Schematic representations of two main schemes used for adsorption of pollutants from wastewaters: batch process and continuous process



continuously in fixed-bed reactors or columns (Volesky and Holan 1995; Volesky 2001; Crini 2003; Ali 2014). Fixed-bed reactors or dynamic continuous-flow systems are commonly used in the industrial world, while batch methods are preferred on the laboratory scale because, apart from their simplicity and ease of operation, they are limited to the treatment of small volumes of solution. Fixed-bed systems have an important advantage because adsorption depends on the concentration of the solute in the solution being treated (Ali 2014). The adsorbent is continuously in contact with fresh solution; hence, the concentration in the solution in contact with a given layer of adsorbent in a column is relatively constant. Conversely, the concentration of adsorbate in contact with a given quantity of adsorbent, as in a batch system, is continuously changing due to the adsorbate being adsorbed (McKay 1996). Other advantages of employing fixed-bed columns for industrial adsorption processes are higher residence times and better heat and mass transfer characteristics than batch reactors.

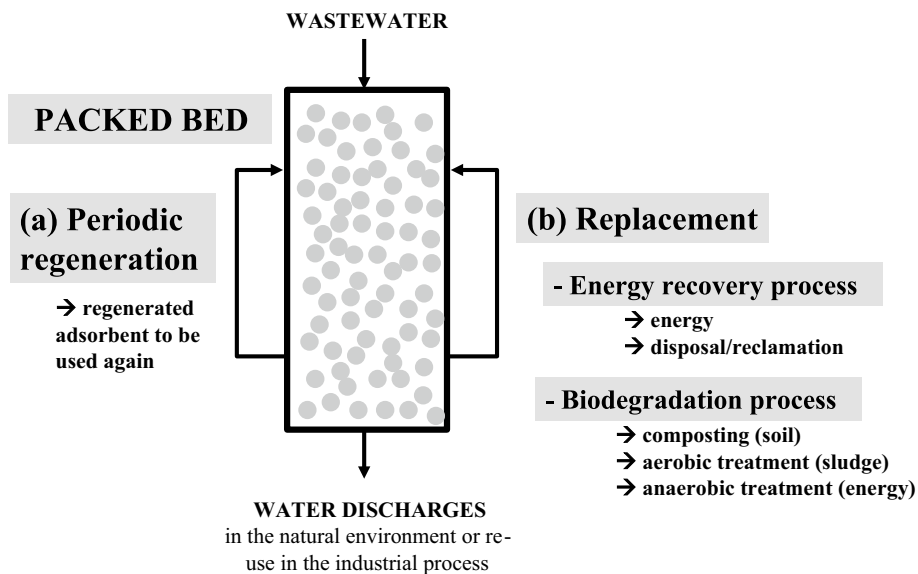
Batch methods are also widely used because this technology is cheap and simple to operate and, consequently, often favored for small- and medium-size process applications

using simple and readily available mixing tank equipment. Simplicity, well-established experimental methods, and easily interpretable results are some of the main reasons frequently evoked for the extensive use of these methods. Another interesting advantage is the fact that, in batch systems, the parameters of the solution/effluent such as contact time, pH, strength ionic and temperature can be controlled and/or adjusted.

Desorption of contaminants

It is important to point out that adsorption using batch systems is a nondestructive technique involving only a phase change of contaminants and hence imposes further problems in the form of sludge disposal. For fixed-bed reactors, Fig. 3 shows two main strategies (regeneration step and replacement) that could be used to deal with spent adsorbent after its usage. One of the important characteristics of a solid material is whether it can be regenerated if necessary. The regeneration of the adsorbent may be crucially important for keeping the process costs down and opening the possibility of recovering the contaminant extracted from the solution.

Fig. 3 The two main strategies, regeneration step and replacement, that can be used to treat spent adsorbent after its usage



For this purpose, it is desirable to desorb the adsorbed contaminants and to regenerate the material for another cycle of application. Desorption studies also reveal the mechanism of adsorption. However, except for commercial activated carbons and organic resins, this aspect has not been adequately studied and there is little literature focusing on this topic.

Control adsorbent performance

In an adsorption-oriented process, separation is defined as a system that transforms a mixture of substances into two or more products that differ from each other in composition. The process is difficult to achieve because it is the opposite of mixing, a process favored by the second law of thermodynamics. For many separation processes, the separation is caused by a mass separating agent, the solid material or adsorbent (King 1980; McKay 1996; Yang 2003). Consequently, the performance of any adsorptive separation or purification process is directly determined by its quality. So, the first important step to an efficient adsorption process is the search for a solid material with high capacity, selectivity and rate of adsorption.

In principle, as adsorption is a surface phenomenon, any porous solid having a large surface area may be an adsorbent (McKay 1996). Other requirements to be taken into account in choosing a material are based on the following criteria: low cost and readily available, suitable mechanical properties, high physical strength (not disintegrating) in solution, a long life, able to be regenerated if required, etc. The data from the literature show that the control of adsorption performances of a solid material in liquid-phase adsorption depends on the following factors: (1) the origin and nature of the solid such as its physical structure, e.g. particle size, specific surface area and porosity, chemical nature

and functional groups, e.g., surface charge, pH at the point of zero charge, and mechanical properties; (2) the activation conditions of the raw solid, e.g., physical treatment, chemical modification; (3) the influence of process variables used in the contacting system such as contact time, initial pollutant concentration, solid dosage and stirring rate; (4) the chemistry of the pollutants, for instance, for a dye molecule, its pK_a , polarity, size and functional groups; and finally, (5) the solution conditions, referring to its pH, ionic strength, temperature, presence of multi-pollutant or impurities, and its variability (Crini 2005, 2006; Park et al. 2010; Crini and Badot 2010).

Types of materials for contaminant removal

Adsorbents classification

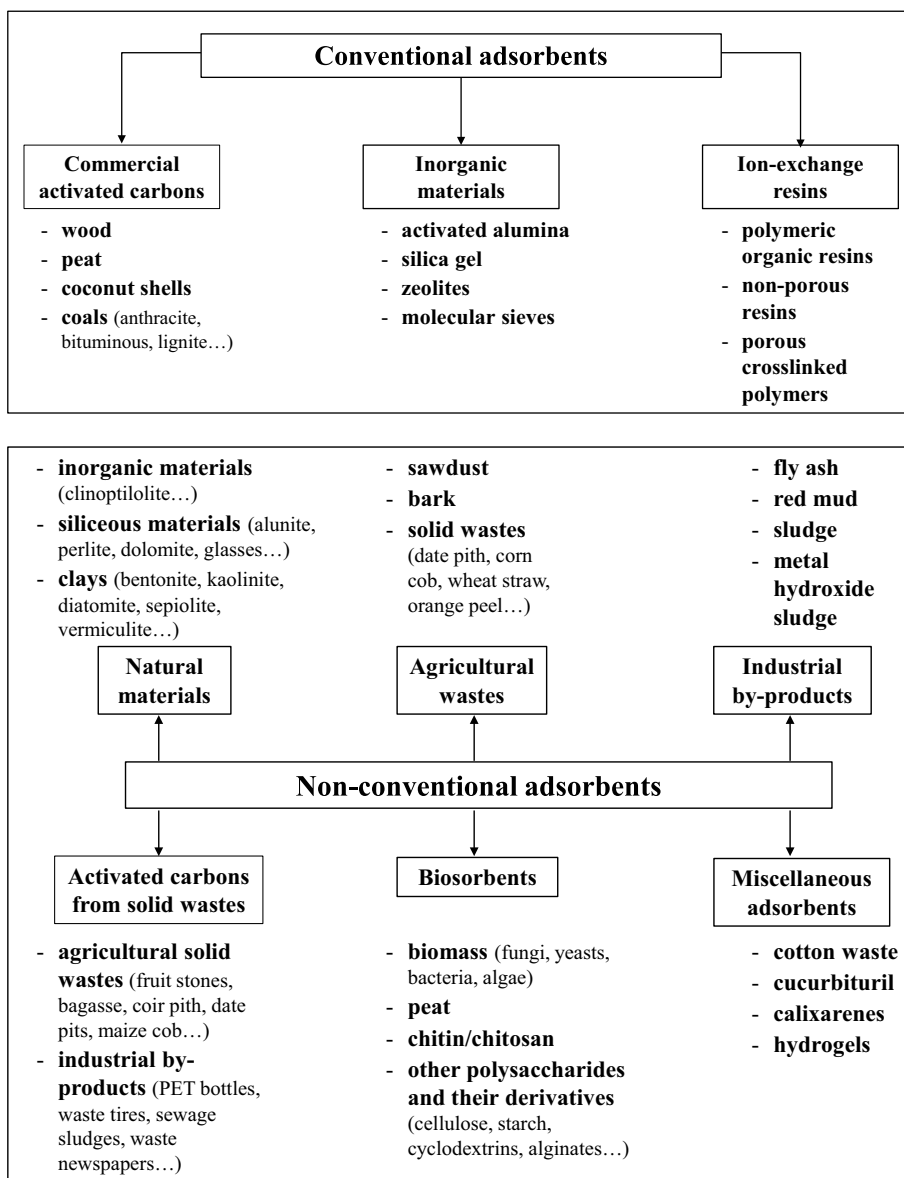
Solid materials used as adsorbents can take a broad range of chemical forms and different geometrical surface structures. This is reflected in the range of their applications in industry, or helpfulness in laboratory practice. Adsorbents can be usually classified in five categories: (1) natural materials such as sawdust, wood, fuller's earth or bauxite; (2) natural materials treated to develop their structures and properties such as activated carbons, activated alumina or silica gel; (3) manufactured materials such as polymeric resins, zeolites or aluminosilicates; (4) agricultural solid wastes and industrial by-products such as date pits, fly ash or red mud; and (5) biosorbents such as chitosan, fungi or bacterial biomass. Another classification was introduced by Dąbrowski (2001) as given in Table 1. Another simplified classification, introduced by Crini (2005, 2006; Crini and Badot 2007), can be used as follows: conventional and non-conventional

Table 1 Basic types of industrial adsorbents

Carbon adsorbents	Mineral adsorbents	Other adsorbents
Activated carbons	Silica gels	Synthetic polymers
Activated carbon fibers	Activated alumina	Composite adsorbents (mineral carbons)
Molecular carbon sieves	Metal oxides	
Fullerenes	Metal hydroxides	Mixed adsorbents
Carbonaceous materials	Zeolites	
	Clay minerals	
	Pillared clays	
	Inorganic nanomaterials	

adsorbents. The list of conventional commercial adsorbents includes activated carbons, ion-exchange resins (polymeric organic resins) and inorganic materials such as activated aluminas, silica gel, zeolites and molecular sieves (which are formally not zeolites) (Fig. 4). Only four types of generic adsorbents have dominated the commercial use of adsorption: activated carbons >> zeolites >> silica gel > activated aluminas (Yang 2003). The list of non-conventional adsorbents includes activated carbons obtained from agricultural solid waste and industrial by-products, natural materials such as clays, industrial by-products such as red mud, biosorbents such as chitosan, and miscellaneous adsorbents such as alginates (Fig. 4).

Fig. 4 Conventional and non-conventional adsorbents for the removal of pollutants from wastewaters according to Crini (2005, 2006) and Crini and Badot (2007)



Commercial activated carbons

Many wastewaters contain significant levels of organic and mineral contaminants which are toxic or otherwise undesirable because they create, in particular, odor, bad taste and color (McKay 1996; Kannan and Sundaram 2001; Swami and Buddhi 2006; Crini 2006; Qu 2008). Among the numerous techniques of contaminant removal, liquid–solid adsorption using activated carbons is the procedure of choice and gives the best results as it can be used to remove different types of contaminants (Dubinin 1966; Manes 1998; Dąbrowski 2001; Dąbrowski et al. 2005; Crini and Badot 2008). Indeed, carbons are one of the oldest and most widely used adsorbents in industry. Due to their great capacity to adsorb contaminants, commercial activated carbons are the most effective adsorbents, and if the adsorption system is properly designed they give a good-quality output. This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to vary their properties. The processes that use these usual adsorbents are often carried out in a batch mode, by adding activated carbon to a vessel containing the contaminated solution, or by feeding the solution continuously through a packed bed of carbon.

In general, commercial activated carbons are used as very good adsorbents of organic matter to reduce the organic load in secondary and/or tertiary treatment, for instance, to process heavily polluted effluent characterized by color, chemical oxygen demand and total organic carbon, from the textile industry. They are generally very broad spectrum adsorbents that efficiently eliminate man-made pollutants such as pesticides, aromatic and phenolic derivatives (polycyclic aromatic hydrocarbons, polychlorobiphenyls, etc.), pharmaceuticals, volatile organic compounds, hydrocarbons and surfactants, minerals including metals but also the molecules that discolor water (dyes), or that cause a taste or smell. They also retain toxic organic compounds refractory to treatments upstream, or they finish off the elimination of organic matter before discharge in the tertiary treatment of industrial effluent. Also, macroporous activated carbons can be used as supports for bacteria: The bacteria then degrade part of the adsorbed organic matter (biological elimination) and thus participate in the *in situ* regeneration of the sorbent. This type of treatment is, in general, coupled to an ozonation stage, further improving the performance of the process. Activated carbon biological filters are, for instance, used for the detoxification of effluent loaded with ions (removal of iron, manganese, nitrate) or for the reduction in biochemical oxygen demand, chemical oxygen demand and total organic carbon (Radovic et al. 2000). An additional major advantage of treatment with commercial activated carbons is the fact that no by-products are produced, unlike during treatment

by chemical oxidation. To obtain cost-effective technology (especially in the field of water recycling) activated carbon powder is used in conjunction with an ultrafiltration membrane or with other techniques, such as oxidation. Active carbon competes favorably with nanofiltration and has completely replaced oxidation with ozone.

Although activated carbons have been used for a long time, development is still being pursued, particularly as there is an increasing demand for very clean water. Research, both fundamental and applied, is currently very active concerning (1) the possible use of new precursors for the activated carbons such as agricultural and industrial wastes, water bottles made of polyethylene terephthalate, scrap tyres; (2) the development of novel classes of materials such as activated carbon cloth, nanotubes; (3) understanding the mechanisms of activation, sorption and regeneration (e.g., microwave techniques, techniques not requiring heat) (Mui et al. 2004; Aktas and Ceçen 2007; Dias et al. 2007; Li et al. 2010).

Activated carbon technology also presents several disadvantages. Commercial activated carbon is quite expensive (e.g., the higher the quality, the greater the cost) and non-selective. Different qualities of carbon also exist which vary not only as a function of the raw material used, but also of the carbonization conditions and of the way in which activation is performed (physical or chemical). And yet, even though the high absorbing power of active carbons no longer needs to be proved, not only is there the problem of disposal of spent activated carbons, but there is also the drawback of their rapid saturation, and thus their regeneration. This regeneration step of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. For these reasons, their widespread use is restricted, in particular small- and medium-size enterprises cannot employ such treatment due to high cost.

Other commercial materials

Various studies have been carried out to replace activated carbons by other commercial adsorbent materials (Allen 1996; Allen and Koumanova 2005; Aksu 2005; Crini 2006; San Miguel et al. 2006; Sudha and Giri Dev 2007; Crini and Badot 2007; Tang et al. 2007; Qu 2008; Vijayaraghavan and Yun 2008; Sud et al. 2008; Wan Ngah and Hanafiah 2008). Those adopted on an industrial scale are zeolites, commercial activated alumina, silica gels, ion-exchange resins and sand (Yang 2003; Crini and Badot 2007; Crini 2010). The resins reduce the discharge of polluted water into the environment and are successfully applied, for instance, in the elimination of mineral and organic contaminants including numerous types of dye molecules from rinsing water or polluting metals from pickling baths. The advantages of ion-exchange include no loss of adsorbent on regeneration, reclamation of solvent after use and the removal of soluble

contaminants at trace levels. However, like commercial activated carbons, these materials are not cheap (except sand)—a factor that cannot be ignored.

Non-conventional green adsorbents

Although these commercial materials are preferred conventional adsorbents for contaminant removal, their widespread industrial use is restricted due to high cost. In addition, Streat et al. (1995) previously reported that the use of commercial carbons based on relatively expensive starting materials is unjustified for most pollution control applications and environmental purposes. As such, alternative non-conventional adsorbents, mainly products and by-products of biological (named biosorbents including biomasses), industrial and agricultural origin and from forest industries (green adsorbents), were proposed, studied and employed as inexpensive and efficient adsorbents (Volesky 1990, 2004, 2007; McKay 1996; Varma et al. 2004; Crini 2005, 2006; Gérente et al. 2007; Li et al. 2008; O'Connell et al. 2008; Oliveira and Franca 2008; Gadd 2009; Crini and Badot 2010; Elwakeel 2010; Sanghi and Verma 2013). These include algae, bacteria, fungi, and yeasts, bark, sawdust, peat, natural products (e.g., cotton, flax, hemp), polysaccharides such as starch, cellulose, chitosan and alginates, industrial by-products (e.g., red mud, sludge), plants and innovative nanomaterials.

All these non-conventional materials are interesting due to the fact that they are abundant in nature, available in large quantities, inexpensive, and may have potential as complexing materials due to their physicochemical characteristics and particular structure. However, it is important to point out that the adsorption processes using these materials are basically at the laboratory stage in spite of unquestionable progress (Gadd 2009; Crini and Badot 2010).

Which is the best non-conventional adsorbent?

Since the range of non-conventional adsorbents proposed in the literature is extremely extensive, attempting to provide a comprehensive list of potential effective materials would be unrealistic. For instance, agricultural wastes and by-products from forest industries include tea waste, coffee, hazelnut shells, peanut hull, sawdust, barks, palm kernel husk, coconut husk, peanut skins, cellulosic and lignocellulosic wastes, hemp-based products, cotton and modified cotton, corncobs, rice hulls, apple wastes, wool fibers, olive cake, almond shells, cactus leaves, banana and orange peels, sugar beet pulp, palm fruit bunch, maize leaf and other different by-products. Adsorption onto these biosorbents has been the focus of much attention, and abundant data on their performance can be found in the literature (Sharma 2015; Crini 2015; Vandenbossche et al. 2015; Khalaf 2016; Morin-Crini and Crini 2017). In Table 2, we reported the features,

advantages and limitations of some selected non-conventional and conventional adsorbents (Crini 2005, 2015; Allen and Koumanova 2005; Crini and Badot 2007, 2008, 2010; Bhattacharyya and Gupta 2008; Wang and Peng 2010). Which is the best adsorbent? There is no direct answer to this question because each adsorbent has advantages and drawbacks (Crini 2006; Gadd 2009).

The comparison of adsorption performance depends on several parameters, and a direct comparison of data obtained using different materials is not possible since experimental conditions are not systematically the same. Most of the information is related to a single contaminant removal individually in batch experiments and little or no data on the removal of contaminants in complex form in real wastewater. Other factors such as operation difficulty, practicability, regeneration potential and environmental impact need to be taken into consideration when selecting one adsorbent over another. Due to the scarcity of consistent cost information, cost comparisons are also difficult to estimate.

Generally, the adsorption capacity exhibited by each material relates primarily to its textural and chemical properties. It is also important to point out that a particular non-conventional adsorbent is only applicable to a particular class of contaminants. Thus, using only one type of material is difficult for the treatment of the complex mixtures of pollutant wastewaters. For instance, bentonite is an ineffective adsorbent for nonionic organic compounds in water. Chitosan without chemical modification is also ineffective for the removal of cationic dyes. Red mud, alumina, zeolite, calcite and clay have been proposed for fluoride removal, but, with fluoride concentration decreasing, these materials lose the fluoride removal capacity. Inherent limitations of raw clays as adsorbents of metals are their low loading capacity, relatively small metal ion binding constants and low selectivity to the type of metal.

Despite the number of papers published on conventional and non-conventional adsorbents for pollutant removal from contaminated solutions, there is as yet little literature reporting a full study of comparisons between materials. The data have not been compared systematically with commercial activated carbons or synthetic ion-exchange resins which show high removal efficiencies and rapid kinetics. Finally, despite continuing dramatic increases in published research, there has been little or no exploitation in an industrial context.

Mechanisms of adsorption

In the context of adsorption, the major challenge is to select the most promising types of adsorbent, mainly in terms of low cost, high capacity (often expressed by the q_{\max} value), high adsorption rate, high selectivity and rapid kinetics. The next real challenge is to clearly identify the

Table 2 Principal commercial, conventional and emerging materials for contaminant removal by adsorption and/or ion-exchange processes

Adsorbent	Features/advantages/mechanisms	Limitations/comments
Activated carbons	The most effective adsorbents in industry (charcoal is the oldest material known in wastewater)	Initial cost of the carbon
Powder activated carbon (PAC)	Porous adsorbents with large surface area	The higher the quality, the greater the cost
Granular activated carbon (GAC)	Versatile material	Performance is dependent on the type of carbon used
Other forms	Two main forms: powdered (PAC) forms to be used in batch experiments followed by filtration and granular (GAC) forms for use in column (more adaptable to continuous contacting)	Non-selective process
	PAC: used in batch experiments due to low capital cost and lesser contact time requirements	Problems with hydrophilic substances
	Widely applied in the treatment of (drinking) water and wastewater	Ineffective against As(III), disperse and vat dyes
	Great capacity to adsorb a wide range of pollutants including metals and metalloids (As(V)), dyes, phenols and chlorophenols, pesticides, and pharmaceuticals and drugs	Require complexing agents to improve their removal performance
	Extensively used for organic contaminant removal (chemical oxygen demand, biochemical oxygen demand, and total organic carbon removal)	Many problems connected with regeneration (large capital investments, expensive steps, loss of adsorbent)
	High capacity and high rate of adsorption	GAC regeneration is easier than PAC
	Fast kinetics	Identification of adsorption mechanisms (in particular for modified activated carbons)
	Produce a high-quality treated effluent	
	Interesting technology in combination with other techniques (precipitation, sand filtration, ion-exchange) or in conjunction with microorganisms	
	Physisorption mechanisms	
Activated carbons from solid wastes	Inexpensive and renewable additional sources of carbon	The performance depends on the raw material, the history of its preparation and treatment conditions
Agricultural wastes	A potential alternative to existing CAC	Reactivation results in a loss of the carbon
Wood wastes	Interesting properties in terms of surface chemistry, surface charge and pore structure like CAC	Laboratory stage
City wastes	Efficient for a large range of pollutants	Identification of adsorption mechanisms
Industrial by-products	A very common adsorbent, mainly in granular form, used in pre- or post-treatment	Construction cost depending on kinds of filters and technologies (rapid or slow processes)
Sand	Well-known filtration technique	Requires a pre-treatment (pH adjustment, coagulation, flocculation) and also a post-treatment (disinfection)
	Large choice of filtration medium with a wide variety in size and specific gravity	Filters become clogged with flocs after a period in use
	Rapid and efficient for SS removal	Frequent cleaning required (every 24–72 h)
	No limitations regarding initial turbidity levels (if coagulant or flocculant is correctly applied)	Cost of energy (regeneration) and cost for treatment of generated sludge
	Widely applied for treating large quantities of drinking water	Not effective for viruses, fluoride, arsenic and salts

Table 2 (continued)

Adsorbent	Features/advantages/mechanisms	Limitations/comments
Activated alumina	Somewhat effective for odor, taste, bacteria and organic matter	
Bauxite	Rapid cleaning time Interesting as pre-treatment in combination with CAC treatment Physorption and diffusion mechanisms Relatively well-known and commercially available Highly porous materials with a high surface area and an interesting distribution of both macro- and micropores Used mainly as desiccants	Cost of the adsorbent pH dependent Requires a pre-treatment to prevent clogging of the material bed when the water contains SS or to remove certain ions
Zeolites	Efficient filter for fluoride, selenium and arsenic removal Also interesting for the treatment of copper, zinc, mercury, uranium and phosphates Classified by the USEPA as among one of the best available technologies for arsenic removal in drinking water The presence of impurities (iron, etc.) do not affect the performance Easily available and relatively cheap (the price depends on the quality of zeolite)	Fluoride removal: regeneration is often required to make it cost-effective Arsenic removal: needs replacement after four or five regeneration Can accumulate bacteria Use of strong acid and base solutions for regeneration step More than 40 natural species: adsorption properties depend on the different materials
Aluminosilicates	40 natural and over 100 synthetic materials; clinoptilolite: the most abundant and frequently studied mineral	Not suitable for reactive dyes
Clinoptilolite	Highly porous aluminosilicates with different cavity structures and unique surface chemistries (a three-dimensional framework having a negatively charged lattice) and valuable physicochemical properties (cation exchange, molecular sieving, catalysis and adsorption)	Low permeability
Chabazite	Suitable adsorbents for dyes, metals, phenols and chlorophenols: high ion-exchange capacity and high selectivity	Complex adsorption mechanism
Modified materials	A high capacity to be easily regenerated (while keeping their initial properties) Main applications: softening and deionization of water, waste treatment, purification of products Ion-exchange mechanism	Requires chemical modification
Silica	A very common adsorbent, mainly in granular form	Cost of the adsorbent
Silica gel	A highly porous solid with mechanical stability	Hydrophilic material
Silica beads	High surface area	Low values for the pH of point of zero charge
Glasses	Numerous industrial environmental applications	High affinity for water (silica gel is a drying agent)
Silica modified	Efficient for removal of organics (toluene, xylene, dyes)	Low resistance toward alkaline solutions
Hybrid materials	Very high adsorption capacities (acid dyes) Physisorption and chemisorption (ion-exchange) mechanisms Abundant, available and low-cost inorganic materials	Requires chemical modification Important role of the pH of the solution
Siliceous materials		

Table 2 (continued)

Adsorbent	Features/advantages/mechanisms	Limitations/comments
Alumite	Porous texture with high surface area	Requires physical and chemical modification
Perlite	Regeneration (alumite) is not necessary	Variable differences in composition (perlite)
Dolomite	Promising adsorbent for dyes	Results depend on the types of perlite used (expanded and unexpanded) and on its origin
Diatomite	Perlite: an amorphous siliceous mineral, inexpensive and easily available in many countries Dolomite: a common double-carbonate mineral consisting of alternative layers of calcite and magnesite Chemisorption mechanism	
Clays	Natural well-known minerals (several classes of clays)	Not efficient for pollutants having a strong acid character
Montmorillonite	Low cost and abundance on most continents	Requires chemical modification or activation (bentonite)
Bentonite	Layered structures with large surface area and high porosity, and high chemical and mechanical stability	Results are pH dependent
Fuller's earth	Strong candidates for ion-exchange (high cation exchange capacity)	Identification of adsorption mechanism (for modified materials)
Sepiolite	Considered as host materials with a strong capacities to adsorb positively charged species; they can also adsorb anionic and neutral species	
Kaolinite	Efficient for basic dyes, phenols and metal ions	
Modified materials	High adsorption capacities with rapid kinetics Montmorillonite: clay with the largest surface area and the highest cation exchange capacity Fuller' earth: a natural clay with an open porous structure	
Commercial polymeric organic resins and synthetic organic resins	Bentonite: a fine powder clay with a high surface area and an efficient sorbent for acid, basic and disperse dyes (very interesting material when coupled with ultrafiltration) Organobentonites: powerful adsorbents Formation of dye-clay complex or organoclay	Derived from petroleum-based raw materials
Porous cross-linked polymers	Established treatment process A large choice of commercially available materials: regular spherical beads with high surface area, a wide range of pore structure, high mechanical strength and high chemical resistance, and with chelating properties, comparable with those of AC	Commercial resins are quite expensive
Macroporous copolymers	Industrial use for adsorption and ion-exchange processes	Sensitive to particle, suspended solids, chemical oxygen demand and oils
Hypercross-linked polymers	Effective materials produce a high-quality treated effluent	Performance is dependent on the type of resin used
Organic resins	High adsorption capacities toward target pollutant including phenolic derivatives, metals, ionic contaminants (fluorides, etc.) and dyes	Incapable of treating large volumes
Chelating polymers	Very interesting technology in combination with CAC treatment	pH dependence
Hydrogels	Economically valid for precious metal recovery	Poor contact with aqueous pollution

Table 2 (continued)

Adsorbent	Features/advantages/mechanisms	Limitations/comments
Synthetic- or natural-based polymers	Can remove unwanted molecules to lower concentrations than CAC does No loss of material on regeneration Organic resins: mechanism due to ion-exchange and/or diffusion into the porous network Hydrogels (super-swelling polymers): Mechanisms involve both electrostatic interactions and diffusion into the three-dimensional polymeric structures	Requires a modification for enhancing the water wettability Non-selective process (conventional resins) Not effective for all dyes (disperse dyes)
Industrial by-products	Low-cost materials and local availability	Adsorption properties strongly depend on the different materials (fly ash, red mud)
Fly ash	Effective for metal and dye removal with interesting adsorption capacities	Contain hazardous substances (coal fly ash may contain harmful metal oxides)
Red mud	Fly ash: a waste material produced in great amounts in combustion processes	Low surface area
Metal hydroxide sludge	Metal hydroxide sludge: a low-cost waste material from the electroplating industry containing insoluble metal hydroxides and salts (calcium, sodium)	Require physical and chemical modifications (red mud)
Blast furnace slag and sludge	Red mud: efficient for metalloids and anions removal	Results are pH dependent (metal hydroxide sludge)
Etc.	Ion-exchange mechanism and/or diffusion	Influence of salts (metal hydroxide sludge)
Agricultural solid wastes and by-products from forest industries	Cheap and readily available resources	Adsorption properties depend on the different materials
Sawdust	Effective for many types of pollutants and pollution (metals, dyes, oils, salts)	Adsorption mechanism must be clarified (bark)
Bark	Bark: a polyphenol-rich material containing a high tannin content	Results are pH dependent
Date pits	Sawdust: an abundant by-product available in large quantities at zero or negligible price containing various organic compounds with polyphenolic groups	Require chemical pre-treatment to improve the adsorption capacity and enhance the efficiency (sawdust)
Pith	Possible regeneration (sawdust)	
Biomass	Physisorption and chemisorption (ion-exchange, hydrogen bonding) mechanisms	Slow process and limiting pH tolerance (algae)
Dead or living biomass	Interesting competitive, cheap and effective technology Simplicity, versatility, flexibility for a wide range of applications	Performance depends on the biomass species (algal species), differences in the cell wall composition of the species, cell size and morphology, and on some external factors (pH, salts, competitive adsorption, metal speciation, temperature)
Fungi	Availability of different biomasses in large quantities and at low cost	Results depend on the functional groups present in the biomass
Algae	Effective and selective adsorbents containing a variety of functional groups: more selective than traditional ion-exchange resins and CAC	Not appropriate for column systems (an immobilization step is necessary for use in column reactors)
White-rot fungi	Important adsorption capacities reported for metal ions and dyes	Technologies are still being developed

Table 2 (continued)

Adsorbent	Features/advantages/mechanisms	Limitations/comments
Yeasts	Suitable for a wide range of metal concentrations from 100 ppm to 100 ppb or even less (algae)	
Agricultural wastes	Fungi can reduce pollutant concentrations to ppb levels	
Food processing	Regeneration is not necessary	
Aquatic plants	Physorption and chemisorption mechanisms	
Publicly acceptable		
Peat	Plentiful, inexpensive and widely available biosorbent	Low mechanical strength
Raw material	A porous and complex soil material with a polar character	A high affinity for water
Modified materials	A low-grade carbonaceous fuel containing lignin, cellulose and humic acids	Poor chemical stability
	Excellent adsorption and ion-exchange properties (contains various functional groups); good adsorption capacities for a variety of organic and inorganic pollutants, particularly effective adsorbent for basic dyes and metal ions	A tendency to shrink and/or swell
	Chemisorption mechanisms	
Chitosan	Abundant, renewable, biodegradable and environmentally friendly resource	Requires a pre-treatment or a chemical activation step
	Chitin, the second most abundant natural polysaccharide next to cellulose, is fairly abundant (found in the exoskeleton of shellfish and crustaceans) and is considered as a by-product of food processing	Influence of some factors (pH, agitation speed, initial dye concentration)
	Low-cost biopolymer and extremely cost-effective	Nonporous material
	Hydrophilic biopolymer with high reactivity and cationic properties in acidic medium	Low surface area
Chitin and derivatives	Excellent diffusion properties	
	Versatile materials (powders, gels, beads, fibers, etc.) with excellent chelation and complexation behavior	Performance depends on the origin of the polysaccharide, the degree of N-acetylation and the treatment of the polymer
Chitosan-based derivatives	Outstanding metal-binding capacities (useful for the recovery of valuable metals) and extremely high affinities for many classes of dyes	Variability in the polymer characteristics and in the materials used
	High efficiency and selectivity in detoxifying both very dilute and concentrated effluents; a high-quality treated effluent is obtained	Not effective for cationic dyes (except after derivatization)
	Easy regeneration if required	Requires chemical modification to improve both its performance and stability
	Physorption (van der Waals attraction, hydrogen bonding, Coulombic attraction) and chemisorption (chelation, complexation) mechanisms	Results depend on the functional groups grafted
Miscellaneous adsorbents	Renewable resources (starches, cotton waste, cellulose), economically attractive and feasible	Results are strongly pH dependent
	Remarkably high swelling capacity in water	Hydrogels: not appropriate for column systems (except for cross-linked beads)
Cellulose		Cost (calixarenes, cucurbiturils, cyclodextrins)
		Low mechanical strength

Table 2 (continued)

Adsorbent	Features/advantages/mechanisms	Limitations/comments
Starch	Relatively low-cost materials with good adsorption capabilities for a variety of pollutants (can reduce pollutant concentrations to ppb levels)	Low surface area
Cyclodextrin	Good removal of a wide range of contaminants	Variability in the materials used
Alginates	Capable of forming host-guest complexes (cyclodextrins, calixarenes, cucurbituril)	A high affinity for water
Cotton waste	Starch: the most abundant carbohydrate (next to cellulose) with numerous biological and chemical properties—abundant biopolymer and widely available in many countries	Poor chemical stability
Calixarenes	Cyclodextrins: natural macrocyclic oligomers having a hydrophobic cavity and a amphiphilic character; exhibit high adsorption capacities toward organic species	A tendency to shrink and/or swell
Cucurbiturils	Cucurbituril: macrocyclic ligand with interesting complexing properties; a high capacity to adsorb (textile) dyes and lanthanide cations Chemisorption mechanism (complexation, inclusion complex formation, ion-exchange)	Not appropriate for column systems (hydrodynamic limitations, column fouling, technical constraints) Requires pre-treatment and/or chemical modification

Cucurbituril: dissolution problem

adsorption mechanism(s), in particular the interactions occurring at the adsorbent/adsorbate interface (Veglio' and Beolchini 1997; Crini 2005). This is an important topic because the adsorption mechanisms involved in contaminant uptake can orientate the design of the desorption strategy (for example, the recovery of certain contaminants such as “precious” metal ions is also an important parameter for the economics of the process).

Despite the large number of papers devoted to the adsorption of contaminants onto conventional or non-conventional adsorbents, most focus on the evaluation of adsorption performances and only a few aim at gaining a better understanding of adsorption mechanisms (Veglio' and Beolchini 1997; Crini 2005). These mechanisms are not fully understood because a large number of interactions are possible. Some of the reported interactions include (Crini 2005): physisorption (physical adsorption), surface adsorption, van der Waals interactions, hydrogen bonding, electrostatic interactions (attraction interactions), ion-exchange, complexation (coordination), chelation, acid-base interactions, proton displacement, precipitation (surface precipitation, microprecipitation), hydrophobic interactions (π - π interactions, Yoshida's interactions), oxidation/reduction, inclusion complex formation, diffusion into the network of the material and covalent binding.

An interesting question remains: Must all these interactions be taken into account to explain the adsorption mechanism? The answer to this question is not so easy. In an oriented adsorption process using a given adsorbent, it is possible that more than one of these interactions can occur simultaneously depending on the composition of the material, the contaminant structure and its properties, and the solution conditions (pH, ionic strength, temperature).

Crini reported the simplified classification of contaminant adsorption mechanisms described in Fig. 5 (Crini 2005, 2006, 2010; Crini and Badot 2007). Four main mechanisms have been proposed, namely physisorption, chemisorption, ion-exchange and precipitation. Some authors consider ion-exchange process as a chemisorption mechanism. Davis et al. (2003) reported that the term ion-exchange does not explicitly identify the binding mechanism; rather, it is used as an umbrella term to describe the experimental observations. The use of the “microprecipitation” term is also a source of debate. This term is used to indicate precipitation taking place locally at the surface of a biosorbent due to particular conditions. A discussion on these terms can be found in the recent review by Robalds et al. (2016). Other classifications of contaminant adsorption mechanisms can be found in the following references: Veglio' and Beolchini (1997), Srivastava and Goyal (2010), Naja and Volesky (2011), Asgher (2012), Michalak et al. (2013) and Robalds et al. (2016).

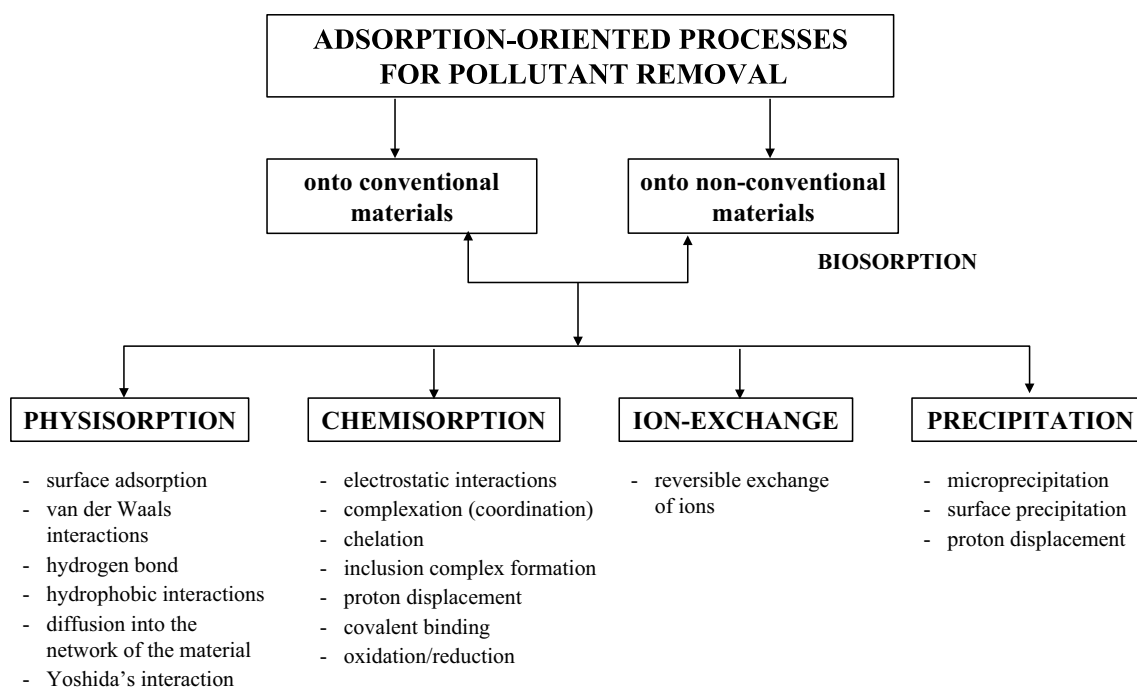


Fig. 5 Classification of pollutant adsorption mechanisms according to Crini (2005, 2006) and Crini and Badot (2007)

Literature based on commercial activated carbons clearly shows a greater number of studies on the adsorption of organic compounds as compared with the inorganic ones, and it is well known that carbon adsorbents are very versatile due to their high surface area, well-developed pore structure and surface properties (Radovic et al. 1997, 2000; Ania et al. 2002). The main mechanism is physisorption. However, although extensive experimental and modeling studies on activated carbons have been reported, the subject remains highly controversial as described by Radovic et al. (2000). Much confusion exists in the literature, especially on the role of surface oxygen functions in the adsorption of aromatic compounds (Moreno-Castilla et al. 1995; Radovic et al. 2000; Pereira et al. 2003).

For biosorbents, the adsorption mechanism is yet not fully understood although some are now well accepted. In the case of biosorption of metals by biomass, the mechanisms can be viewed as being extracellular or occurring discretely at the cell wall. Intracellular adsorption would normally imply bioaccumulation by a viable organism. Gadd (1990), Veglio' and Beolchini (1997), Volesky (2001) and Aksu (2005) previously discussed various mechanisms involved in biosorption using microorganisms (fungi, yeasts or bacteria, etc.). Gadd (1990) commented that "a large variety of physical, chemical and biological mechanisms may be involved, including adsorption, precipitation, complexation and transport." In general, two different metal-binding mechanisms have been postulated to be active in biosorption pollutant uptake: (1) chemisorption by ion-exchange,

complexation (including coordination) and/or chelation (biosorption process), and (2) physical adsorption and/or (micro)precipitation (in this case, the process is termed bioaccumulation). Other interactions have been proposed, including metabolism-dependent transport, adsorption of simple ionic species, hydrogen bonding interactions, biological mechanisms, reactions involving hydrolysis products of metal ions or oxidation/reduction.

Accumulation of metals and radionuclides by algae can be described as being composed of two phases: a rapid phase of metabolism-independent binding to the cell surface (biosorption) followed by a slower phase due to simultaneous effects of growth and surface adsorption, active or intracellular uptake by passive diffusion (Garnham 1997). Biosorption- and bioaccumulation-based mechanisms have been adopted for the description of the mechanistically different types of metal sequestering by microorganisms. However, the nature of the binding processes in biosorption is yet complex and unknown, due to the complexity of most biopolymers.

Numerous authors accept that the decolourization process using non-conventional materials generally results from two main mechanisms—adsorption and ion-exchange (Allen and Koumanova 2005; Crini 2006), and is influenced by many factors including the type of adsorbents/biosorbents and dyes, and the process variables. For instance, ion-exchange and hydrogen bonding interactions are the main mechanisms for the removal of metals by sawdust (Shukla et al. 2002). The cell walls of sawdust mainly consist of cellulose and

lignin, with many hydroxyl groups such as those on tannins or other phenolic compounds. All these components are active ion-exchange compounds.

Polysaccharide-based materials are mainly used as a chelating or complexing ion-exchange media. These biopolymers (i.e., starch, cellulose, chitin and alginates) and their derivatives (e.g., chitosan, cyclodextrin) contain a variety of functional groups, which can chelate ionic species of a specific size and charge. Such materials are thus often much more selective than traditional ion-exchange resins and can reduce heavy metal ion concentrations to ppb levels (Kentish and Stevens 2001; Crini and Badot 2008). Crini (2015), reviewing dye removal by starch-based materials reported that the adsorption mechanisms were not fully understood because numerous interactions were possible, including ion-exchange, acid–base interactions, precipitation, hydrogen bonding, hydrophobic interactions and physisorption.

For cyclodextrin-based adsorbents, inclusion complex formation and diffusion into the polymer network are the preferred concepts in biosorption because they account for many of the observations made during contaminant uptake studies (Crini 2014). In a comprehensive review, Morin-Crini et al. (2018) recently reported that, in spite of the abundance of literature and conclusive results obtained at the laboratory scale, interpreting the mechanism of pollutant elimination remains an interesting source of debate and sometimes of contradiction.

Plant fibers used as biosorbents consist mainly of cellulose, hemicelluloses, lignin and some pectin and extractives (fats, waxes, etc.). Metal ions mainly adsorb carboxylic (primarily present in hemicelluloses, pectin and lignin), phenolic (lignin and extractives) and to some extent hydroxyl (cellulose, hemicelluloses, lignin, extractives and pectin) and carbonyl groups (lignin). Strong bonding of metal ions by the hydroxyl, phenolic and carboxylic groups often involves complexation and ion-exchange (Crini and Badot 2010).

Conclusion

Preserving the environment, and in particular the problem of water contamination, has become a major preoccupation for everyone—the public, industry, scientists and researchers as well as decision-makers on a national, European, or international level. The public demand for pollutant-free waste discharge to receiving waters has made decontamination of industrial wastewaters a top priority. This is a difficult and challenging task. It is also difficult to define a universal method that could be used for the elimination of all contaminants from wastewaters. Among the numerous and various treatment processes currently cited for wastewater treatment, only a few are commonly used by the industrial sector. However, it is now accepted that adsorption is the procedure of

choice and gives the best results as it can be used to remove many different types of contaminants.

In this chapter, a general overview on adsorption processes for contaminant removal has been presented, including a classification for the different types of conventional and non-conventional adsorbents used for this purpose and the interactions proposed to explain adsorption mechanisms. Commercial activated carbon is extensively used not only for adsorbing contaminants from drinking water sources, but also for removing pollutants from wastewater streams. Other conventional materials include organic resins, activated alumina, zeolites and sand. Non-conventional adsorbents can be also obtained and employed as low-cost and efficient solid adsorbents. These materials have not yet been significantly commercialized even though they possess numerous advantages over currently available carbon and organic resins for pollutant removal. Perhaps, one reason why non-conventional adsorbents have not been widely used in industry is the lack of knowledge about the engineering of such materials. We think that, for novel adsorbents to be accepted by industry, it will be necessary to adopt a multidisciplinary approach in which chemists, engineers, material scientists, biologists, microbiologists and computer scientists work together. The opportunity now exists to consider other solid materials such as biomass, cellulose and chitosan for emerging applications. They will undoubtedly be at the center of some extremely profitable commercial activities in the future although their development requires further investigation in the direction of mechanisms (modeling), of regeneration of the adsorbent material (if necessary), and of testing materials with real industrial effluents.

References

- Aksu Z (2005) Application of biosorption for the removal of organic pollutants: a review. *Process Biochem* 40:997–1026. <https://doi.org/10.1016/j.procbio.2004.04.008>
- Aktas Ö, Çeçen F (2007) Bioregeneration of activated carbon: a review. *Int. Biodeterior Biodegrad* 59:257–272. <https://doi.org/10.1016/j.ibiod.2007.01.003>
- Ali I (2014) Water treatment by adsorption columns: evaluation at ground level. *Sep Purif Rev* 43:175–205. <https://doi.org/10.1080/15422119.2012.748671>
- Allen SJ (1996) Types of adsorbent materials. In: McKay G (ed) *Use of adsorbents for the removal of pollutants from wastewaters*, chapter 5. CRC Press, Boca Raton, pp 59–97
- Allen SJ, Koumanova B (2005) Decolourisation of water/wastewater using adsorption (review). *J Univ Chem Technol Metall* 40:175–192
- Ania CO, Parra JB, Pis JJ (2002) Influence of oxygen-containing functional groups on active carbon adsorption of selected organic compounds. *Fuel Process Technol* 79:265–271. [https://doi.org/10.1016/S0378-3820\(02\)00184-4](https://doi.org/10.1016/S0378-3820(02)00184-4)
- Asgher M (2012) Biosorption of reactive dyes: a review. *Water Air Soil Pollut* 223:2417–2435. <https://doi.org/10.1007/s11270-011-1034-z>

- Babel S, Kurniawan TA (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *J Hazard Mater* 97:219–243. [https://doi.org/10.1016/S0304-3894\(02\)00263-7](https://doi.org/10.1016/S0304-3894(02)00263-7)
- Bajpai AK, Rajpoot M (1999) Adsorption techniques—a review. *J Sci Ind Res* 58:844–860
- Bhattacharyya KG, Gupta SS (2008) Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. *Adv Colloid Int Sci* 140:114–131. <https://doi.org/10.1016/j.cis.2007.12.008>
- Blackburn RS (2004) Natural polysaccharides and their interactions with dye molecules: applications in effluent treatment. *Environ Sci Technol* 38:4905–4909. <https://doi.org/10.1021/es049972n>
- Cox M, Nègré P, Yurramendi L (2007) Industrial liquid effluents. INASMET Tecnalia, San Sebastian, p 283
- Crini G (2003) Studies on adsorption of dyes on beta-cyclodextrin polymer. *Bioresour Technol* 90:193–198. [https://doi.org/10.1016/S0960-8524\(03\)00111-1](https://doi.org/10.1016/S0960-8524(03)00111-1)
- Crini G (2005) Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog Polym Sci* 30:38–70. <https://doi.org/10.1016/j.progpolymsci.2004.11.002>
- Crini G (2006) Non-conventional low-cost adsorbents for dye removal. *Bioresour Technol* 97:1061–1085. <https://doi.org/10.1016/j.biortech.2005.05.001>
- Crini G (2010) Wastewater treatment by sorption. In: Crini G, Badot PM (eds) Sorption processes and pollution, chap 2. PUF, Besançon, pp 39–78
- Crini G (2014) Review: a history of cyclodextrins. *Chem Rev* 114:10940–10975. <https://doi.org/10.1021/cr500081p>
- Crini G (2015) Non-conventional adsorbents for dye removal. In: Sharma SK (ed) Green chemistry for dyes removal from wastewater. Scrivener Publishing LLC, Beverly, pp 359–407
- Crini G, Badot PM (eds) (2007) Traitement et épuration des eaux industrielles polluées. PUF, Besançon, p 353
- Crini G, Badot PM (2008) Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: a review of recent literature. *Prog Polym Sci* 33:399–447. <https://doi.org/10.1016/j.progpolymsci.2007.11.001>
- Crini G, Badot PM (eds) (2010) Sorption processes and pollution. PUF, Besançon, p 489
- Crini G, Lichtfouse É, Wilson LD, Morin-Crini N (2018) Adsorption-oriented using conventional and non-conventional adsorbents for wastewater treatment. In: Crini G, Lichtfouse É (eds) Environmental chemistry for a sustainable world, green adsorbents for pollutant removal—fundamentals and design, chapter 2, vol 1. Springer, Berlin, pp 23–71. https://doi.org/10.1007/978-3-319-92111-2_2. ISBN 978-3-319-92111-2
- Dąbrowski A (2001) Adsorption—from theory to practice. *Adv Colloid Interface Sci* 93:135–224
- Dąbrowski A, Podkościelny P, Hubicki Z, Barczak M (2005) Adsorption of phenolic compounds by activated carbon—a critical review. *Chemosphere* 58:1049–1070. <https://doi.org/10.1016/j.chemosphere.2004.09.067>
- Davis TA, Volesky B, Mucci A (2003) A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res* 37:4311–4330. [https://doi.org/10.1016/S0043-1354\(03\)00293-8](https://doi.org/10.1016/S0043-1354(03)00293-8)
- Dias JM, Alvim-Ferraz MCM, Almeida MF, Rivera-Utrilla J, Sánchez-Polo M (2007) Waste materials for activated carbon preparation and its use in aqueous-phase treatment: a review. *J Environ Manag* 85:833–846. <https://doi.org/10.1016/j.jenvman.2007.07.031>
- Dubinín MM (1966) Porous structure and adsorption properties of activated carbons. In: Walker PL (ed) Chemistry and physics of carbon, vol 2. Marcel Dekker, New York, pp 51–120
- Elwakeel KZ (2010) Environmental application of chitosan resins for the treatment of water and wastewater: a review. *J Dispers Sci Technol* 31:273–288. <https://doi.org/10.1080/01932690903167178>
- Furuya EG, Chang HT, Miura Y, Noll KE (1997) A fundamental analysis of the isotherm for the adsorption of phenolic compounds on activated carbon. *Sep Purif Technol* 11:69–78
- Gadd GM (1990) Biosorption. *Chem Ind* 13:421–426
- Gadd GM (2009) Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. *J Chem Technol Biotechnol* 84:13–28. <https://doi.org/10.1002/jctb.1999>
- Garnham GW (1997) The use of algae as metal biosorbents. In: Wase J, Forster C (eds) Biosorbents for metal ions, chapter 2. Taylor & Francis Ltd, London, pp 11–37
- Gavrilescu M (2004) Removal of heavy metals from the environment by biosorption. *Eng Life Sci* 4:219–232. <https://doi.org/10.1002/elsc.200420026>
- Gérente C, Lee VKC, Le Cloirec P, McKay G (2007) Application of chitosan for the removal of metals from wastewaters by adsorption—mechanisms and models review. *Crit Rev Environ Sci Technol* 37:41–127. <https://doi.org/10.1080/10643380600729089>
- Gupta VK, Suhas (2009) Application of low-cost adsorbents for dye removal—a review. *J Environ Manag* 90:2313–2342. <https://doi.org/10.1016/j.jenvman.2008.11.017>
- Gupta VK, Nayak A, Agarwal S (2015) Bioadsorbents for remediation of heavy metals: current status and their future prospects. *Environ Eng Res* 20:1–18. <https://doi.org/10.4491/eer.2014.018>
- Harvey PJ, Campanella BF, Castro PM, Harms H, Lichtfouse E, Schäffner AR, Smrcek S, Werck-Reichhart D (2002) Phytoremediation of polyaromatic hydrocarbons, anilines and phenols. *Environ Sci Pollut Res Int* 9:29–47
- Houghton JJ, Quarmby J (1999) Biopolymers in wastewater treatment. *Curr Opin Biotechnol* 10:259–262. [https://doi.org/10.1016/S0958-1669\(99\)80045-7](https://doi.org/10.1016/S0958-1669(99)80045-7)
- Kannan N, Sundaram MM (2001) Kinetics and mechanism of removal of methylene blue by adsorption on various carbons. *Dyes Pigments* 51:25–40. [https://doi.org/10.1016/S0143-7208\(01\)00056-0](https://doi.org/10.1016/S0143-7208(01)00056-0)
- Kentish SE, Stevens GW (2001) Innovations in separations technology for the recycling and re-use of liquid waste streams. *Chem Eng J* 84:149–159
- Khalaf MN (ed) (2016) Green polymers and environmental pollution control. CRC Press, Oakville, p 436
- King CJ (1980) Separation processes, 2nd edn. McGraw-Hill, New York
- Kyzas GZ, Kostoglou M (2014) Green adsorbents for wastewaters: a critical review. *Materials* 7:333–364. <https://doi.org/10.3390/ma7010333>
- Kyzas GZ, Fu J, Matis KA (2013) The change from past to future for adsorbent materials in treatment of dyeing wastewaters. *Materials* 6:5131–5158. <https://doi.org/10.3390/ma6115131>
- Landy D, Mallard I, Ponchel A, Monflier E, Fourmentin S (2012a) Cyclodextrins for remediation technologies. In: Lichtfouse E, Schwarzbauer J, Robert D (eds) Environmental chemistry for a sustainable world: nanotechnology and health risk, vol 1. Springer, Berlin, pp 47–81
- Landy D, Mallard I, Ponchel A, Monflier E, Fourmentin S (2012b) Remediation technologies using cyclodextrins: an overview. *Environ Chem Lett* 10:225–237. <https://doi.org/10.1007/s10311-011-0351-1>
- Li CB, Hein S, Wang K (2008) Biosorption of chitin and chitosan. *Mater Sci Technol* 24:1088–1099. <https://doi.org/10.1179/17438408X341771>
- Li L, Liu S, Zhu T (2010) Application of activated carbon derived from scrap tires for adsorption of Rhodamine B. *J Environ Sci* 22:1273–1280. [https://doi.org/10.1016/S1001-0742\(09\)60250-3](https://doi.org/10.1016/S1001-0742(09)60250-3)
- Lim AP, Aris AZ (2014) A review on economically adsorbents on heavy metals removal in water and wastewater. *Rev*

- Environ Sci Biotechnol 13:163–181. <https://doi.org/10.1007/s11157-013-9330-2>
- Manes M (1998) Activated carbon adsorption fundamentals. In: Meyers RA (ed) Encyclopedia of environmental analysis and remediation, vol 1. Wiley, New-York, pp 26–68
- McKay G (ed) (1996) Use of adsorbents for the removal of pollutants from wastewaters. CRC Press, Boca Raton, p 208
- Michalak I, Chojnacka K, Witek-Krowiak A (2013) State of the art for the biosorption process—a review. Appl Biochem Biotechnol 170:1389–1416. <https://doi.org/10.1007/s12010-013-0269-0>
- Moreno-Castilla C, Ferro-García MA, Joly JP, Bautista-Toledo I, Carrasco-Marín F, Rivera-Utrilla J (1995) Activated carbon surface modifications by nitric acid, hydrogen peroxide, and ammonium peroxydisulfate treatments. Langmuir 11:4386–4392
- Morin-Crini N, Crini G (eds) (2017) Eaux industrielles contaminées. PUF, Besançon, p 513
- Morin-Crini N, Winterton P, Fourmentin S, Wilson LD, Fenyvesi E, Crini G (2018) Water-insoluble β -cyclodextrin-epichlorohydrin polymers for removal of pollutants from aqueous solutions by sorption processes using batch studies: a review of inclusion mechanism. Prog Polym Sci 78:1–23. <https://doi.org/10.1016/j.progpolymsci.2017.07.004>
- Mui ELK, Ko DCK, McKay G (2004) Production of active carbons from waste tyres—a review. Carbon 42:2789–2805. <https://doi.org/10.1016/j.carbon.2004.06.023>
- Naja G, Volesky B (2011) The mechanism of metal cation and anion biosorption. In: Kotrba P, Mackova M, Macek T (eds) Microbial biosorption of metals. Springer, Dordrecht, pp 19–58. https://doi.org/10.1007/978-94-007-0443-5_3
- Ngah WSW, Hanafiah MAKM (2008) Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. Bioresour Technol 99:3945–3948. <https://doi.org/10.1016/j.biortech.2007.06.011>
- O’Connell DW, Birkinshaw C, O’Dwyer TF (2008) Heavy metal adsorbents prepared from the modification of cellulose: a review. Bioresour Technol 99:6709–6724. <https://doi.org/10.1016/j.biortech.2008.01.036>
- Oliveira LS, Franca AS (2008) Low cost adsorbents from agro-food wastes. In: Greco LV, Bruno MN (eds) food science and technology: new research. Nova Publishers, New-York, pp 1–39
- Ong ST, Keng PS, Lee SL, Hung YT (2014) Low cost adsorbents for sustainable dye containing-wastewater treatment. Asian J Chem 26:1873–1881. <https://doi.org/10.14233/ajchem.2014.15653>
- Park D, Yun YS, Park JM (2010) The past, present, and future trends of biosorption. Biotechnol Bioprocess Eng 15:86–102. <https://doi.org/10.1007/s12257-009-0199-4>
- Pereira MFR, Soares SF, Órfão JJM, Figueiredo JL (2003) Adsorption of dyes on activated carbons: influence of surface chemical groups. Carbon 41:811–821. [https://doi.org/10.1016/S0008-6223\(02\)00406-2](https://doi.org/10.1016/S0008-6223(02)00406-2)
- Pollard SJT, Fowler GD, Sollars CJ, Perry R (1992) Low-cost adsorbents for waste and wastewater treatment: a review. Sci Total Environ 116:31–52. [https://doi.org/10.1016/0048-9697\(92\)90363-W](https://doi.org/10.1016/0048-9697(92)90363-W)
- Qu J (2008) Research progress of novel adsorption processes in water purification: a review. J Environ Sci 20:1–13. [https://doi.org/10.1016/S1001-0742\(08\)60001-7](https://doi.org/10.1016/S1001-0742(08)60001-7)
- Radovic LR, Silva IF, Ume JI, Menéndez JA, Leon CA, Leon Y, Scaroni AW (1997) An experimental and theoretical study of the adsorption of aromatics possessing electron-withdrawing and electron-donating functional groups by chemically modified activated carbons. Carbon 35:1339–1348
- Radovic LR, Moreno-Castilla C, Rivera-Utrilla J (2000) Carbon materials as adsorbents in aqueous solutions. Chem Phys Carbon 27:227–405
- Rafatullah M, Sulaiman O, Hashim R, Ahmad A (2010) Adsorption of methylene blue on low-cost adsorbents: a review. J Hazard Mater 177:70–80. <https://doi.org/10.1016/j.jhazmat.2009.12.047>
- Ramakrishna KR, Viraraghavan T (1997) Dye removal using low cost adsorbents. Water Sci Technol 36:189–196. [https://doi.org/10.1016/S0273-1223\(97\)00387-9](https://doi.org/10.1016/S0273-1223(97)00387-9)
- Robalds A, Naja GM, Klavins M (2016) Highlighting inconsistencies regarding metal biosorption. J Hazard Mater 304:553–556. <https://doi.org/10.1016/j.jhazmat.2015.10.042>
- San Miguel G, Lambert SD, Graham NJD (2006) A practical review of the performance of organic and inorganic sorbents for the treatment of contaminated waters. J Chem Technol Biotechnol 81:1685–1696
- Sanghi R, Verma P (2013) Decolorisation of aqueous dye solutions by low-cost adsorbents: a review. Color Technol 129:85–108. <https://doi.org/10.1111/cote.12019>
- Sharma SK (ed) (2015) Green chemistry for dyes removal from wastewater. Scrivener Publishing LLC Wiley, Beverley, p 496
- Shukla A, Zhang YH, Dubey P, Margrave JL, Shukla SS (2002) The role of sawdust in the removal of unwanted materials from water. J Hazard Mater B95:137–152
- Srivastava S, Goyal (2010) Novel biomaterials. Decontamination of toxic metals from wastewater. Springer, New York. <https://doi.org/10.1007/978-3-642-11329-1>
- Streat M, Patrick JW, Perez MJC (1995) Sorption of phenol and parachlorophenol from water using conventional and novel activated carbons. Water Res 29:467–472. [https://doi.org/10.1016/0043-1354\(94\)00187-C](https://doi.org/10.1016/0043-1354(94)00187-C)
- Sud D, Mahajan G, Kaur MP (2008) Agricultural waste material as potential sorbent for sequestering heavy metal ions from aqueous solutions—a review. Bioresour Technol 99:6017–6027. <https://doi.org/10.1016/j.biortech.2007.11.064>
- Sudha S, Giri Dev VR (2007) Low cost-sorbents—an overview. Synth Fibres 36:5–9
- Swami D, Buddhi D (2006) Removal of contaminants from industrial wastewater through various non-conventional technologies: a review. Int J Environ Poll 27:324–346. <https://doi.org/10.1504/IJEP.2006.010576>
- Tang X, Zhang X, Zhou A (2007) Research progresses on adsorbing heavy metal ions with crosslinked chitosan. Ion Exch Sorpt 23:378–384
- Vandenbossche M, Jimenez M, Casetta M, Traisnel M (2015) Remediation of heavy metals by biomolecules: a review. Crit Rev Environ Sci Technol 45:1644–1704. <https://doi.org/10.1080/10643389.2014.966425>
- Varma AJ, Deshpande SV, Kennedy JF (2004) Metal complexation by chitosan and its derivatives: a review. Carbohydr Polym 55:77–93. <https://doi.org/10.1016/j.carbpol.2003.08.005>
- Veglio’ F, Beolchini F (1997) Removal of metals by biosorption: a review. Hydrometallurgy 44:301–316. [https://doi.org/10.1016/S0304-386X\(96\)00059-X](https://doi.org/10.1016/S0304-386X(96)00059-X)
- Vijayaraghavan K, Balasubramanian R (2015) Is biosorption suitable for decontamination of metal-bearing wastewaters? A critical review on the state-of-the-art of biosorption processes and future directions. J Environ Manag 160:283–296. <https://doi.org/10.1016/j.jenvman.2015.06.030>
- Vijayaraghavan K, Yun YS (2008) Bacterial biosorbents and biosorption. Biotechnol Adv 26:266–291. <https://doi.org/10.1016/j.biotechadv.2008.02.002>
- Volesky B (1990) Biosorption of metals. CRC Press, Boca Raton, p 408
- Volesky B (2001) Detoxification of metal-bearing effluents: biosorption for the next century. Hydrometallurgy 59:203–216. [https://doi.org/10.1016/S0304-386X\(00\)00160-2](https://doi.org/10.1016/S0304-386X(00)00160-2)
- Volesky B (2004) Sorption and biosorption. BV-Sorbex Inc, Montreal, p 316

- Volesky B (2007) Biosorption and me. *Water Res* 41:4017–4029. <https://doi.org/10.1016/j.watres.2007.05.062>
- Volesky B, Holan ZR (1995) Biosorption of heavy metals. *Biotechnol Prog* 11:235–250. <https://doi.org/10.1021/bp00033a001>
- Wan Ngah WS, Hanafiah MAKM (2008) Removal of heavy metal ions from wastewater by chemically modified plant wastes as sorbents: a review. *Bioresour Technol* 99:3935–3948. <https://doi.org/10.1016/j.biortech.2007.06.011>
- Wang SB, Peng YL (2010) Natural zeolites as effective adsorbents in water and wastewater treatment. *Chem Eng J* 156:11–24. <https://doi.org/10.1016/j.cej.2009.10.029>
- Wase J, Forster C (1997) *Biosorbents for metal ions*. Taylor & Francis, Bristol, p 249
- Yang TR (2003) *Adsorbents: fundamentals and applications*. Wiley, Hoboken, p 424