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

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# Adsorption-Oriented Processes Using Conventional and Non-conventional Adsorbents for Wastewater Treatment

Grégorio Crini, Eric Lichtfouse, Lee D. Wilson, and Nadia Morin-Crini

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**Abstract** The removal of contaminants from wastewaters is a matter of great interest in the field of water pollution. Amongst the numerous techniques of contaminant removal, adsorption using solid materials (named adsorbents) is a simple, useful and effective process. The adsorbent may be of mineral, organic or biological origin. Activated carbon is the preferred material at industrial scale and is extensively used not only for removing pollutants from wastewater streams but also for adsorbing contaminants from drinking water sources (e.g. rivers, lakes or reservoirs). However, its widespread use is restricted due to high cost. In the last three decades, numerous approaches have been studied for the development of cheaper and more effective adsorbents capable to eliminate pollutants at trace levels. This chapter gives a general overview of liquid-solid adsorption processes using conventional and non-conventional materials for pollutant removal. It outlines some of the principles of adsorption and proposes a classification for the different types of materials. Finally, the chapter discusses different mechanisms involved in the adsorption phenomena.

## Abbreviations

AAS	Atomic absorption spectroscopy
AC	Activated carbons
BOD	Biochemical oxygen demand
CAA	Commercial activated alumina
CAC	Commercial activated carbons
COD	Chemical oxygen demand
DSC	Differential scanning calorimetry
ESR	Electron spin resonance spectroscopy
FT-IR	Fourier transform infrared spectroscopy
GAC	Granular activated carbon
ICP	Inductively coupled plasma
ISE	Ion selective electrode
LC-MS	Liquid chromatography mass spectrometry
NMR	Nuclear magnetic resonance
OM	Organic matter
PAC	Powder activated carbon
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorobiphenyls
PET	Polyethylene terephthalate
PZC	Point of zero charge
SEM	Surface electron microscopy
SMEs	Small and medium-size enterprises
SS	Suspended solids
TGA	Thermogravimetric analysis
TOC	Total organic carbon

VOC	Volatile organic compounds
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy

## 2.1 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 (Berefield et al. 1982; Liu and Liptak 2000; Landy et al. 2012a; 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 approaches, cementation, membrane filtration, phytoremediation, ion-exchange, and carbon adsorption (Berefield et al. 1982; Volesky 1990; Liu and Liptak 2000; 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 (Table 2.1). 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). Consequently, adsorption is of interest to many economic sectors and concerns areas such as chemistry, food and pharmaceutical industries, and the treatment of drinking water and industrial wastewater. Indeed, adsorption is – along with biodegradation – one of the two major treatments applied to the decontamination of water. Adsorption processes are considered the best choice compared to other methods due to their convenience, easy operation and simplicity of design, high efficiency, and also for

**Table 2.1** Fundamental practical applications of adsorption-oriented processes

Separation and purification of gas and liquid mixtures
Drying gases and liquids
Solvent recovery
Purification of air
Separation and purification of chemicals, pharmaceutical and biological substances
Removal of impurities from liquid and gas media
Decolorizing applications
Water purification (pesticides removal, arsenic elimination. ...)
Wastewater decontamination

their wider applicability in water pollution control (McKay 1996; Babel and Kurniawan 2003; Swami and Buddhi 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 produce high quality water, with pollutant concentrations under the legal limits for discharge waters.

In general terms, activated carbons (AC) must be thought of as being most effective adsorbents and, as such, their performance in removing contaminants such as metals, radionuclides, rare earth elements, phenolic and aromatic derivatives (including dyes and pesticides), pharmaceuticals and drugs have been examined widely (Dąbrowski et al. 2005). In addition, in the field of wastewater treatment, adsorption onto commercial AC (CAC) has proved efficient in removing colloidal substances and soluble organic substances that are non-biodegradable or chemically stable like recalcitrant synthetic molecules. Attention has also focused on adsorption onto commercial activated alumina (CAA), 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. Table 2.2 show the top ten most cited reviews in the ISI Web of Science database for 2000–2017 with “Adsorbents”, “Wastewater and “Review” in the topic. The number of reviews appearing with these three terms in the topic in 2017, 2016, 2015, 2014, 2013 and 2012 is 66, 59, 54, 46 and 39, respectively (ISI Web of Science database).

**Table 2.2** The top ten most cited reviews in the ISI Web of Science database for 2000–2017 with “Adsorbents”, “Wastewater” AND “Review” in the topic (out of a total of 383 reviews appearing, December 04, 2017)

1. Crini G (2006) Non-conventional low-cost adsorbents for dye removal. *Bioresource Technology* 97:1061–1085. Times cited: 1989.
2. Babel S, Kurniawan TA (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: A review. *Journal of Hazardous Materials* 97:219–243. Times cited: 1589.
3. Mohan D, Pittman CU (2007) Arsenic removal from waste/wastewater using adsorbents – A critical review. *Journal of Hazardous Materials* 142:1–53. Times cited: 1561.
4. Gupta VK, Suhas (2009) Application of low-cost adsorbents for dye removal – A review. *Journal of Environmental Management* 90:2313–2342. Times cited: 1285.
5. Crini (2005) Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science* 30:38–70. Times cited: 982.
6. Kannan N, Sundaram MM (2001) Kinetics and mechanism of removal of methylene blue by adsorption on various carbons. *Dyes and Pigments* 51:25–40. Times cited: 903.
7. 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. *Progress in Polymer Science* 33:399–447. Times cited: 894.
8. Rafatullah M, Sulaiman O, Hashim R, Ahmad A (2010) Adsorption of methylene blue on low-cost adsorbents: A review. *Journal of Hazardous Materials* 177:70–80. Times cited: 855.
9. Ngah WSW, Hanafiah MAKM (2008) Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresource Technology* 99:3945–3948. Times cited: 639.
10. Wang SB, Peng YL (2010) Natural zeolites as effective adsorbents in water and wastewater treatment. *Chemical Engineering Journal J* 156:11–24. Times cited: 601.

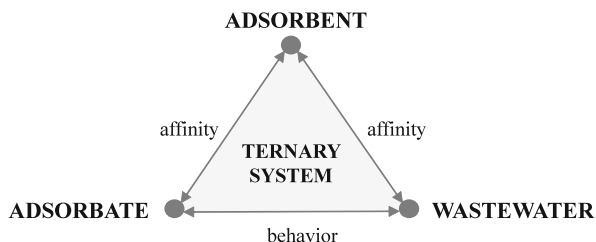
This chapter presents adsorption processes as a decontamination method for the removal of contaminants from synthetic solutions and industrial effluents. It outlines some of the principles of contamination adsorption onto solid materials. The chapter also proposes a classification for the different types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

## 2.2 Wastewater Treatment by Adsorption

### 2.2.1 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 towards the solid phase (Dubinin 1966). This surface phenomenon is a manifestation of complicated interactions among the

**Fig. 2.1** Schema depicting the relationships between the three components of an adsorption system (Crini 2005)



three components involved, i.e. the adsorbent, the adsorbate and the wastewater (e.g. effluent, synthetic solution or water).

Figure 2.1 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.

### ***2.2.2 Adsorption, Sorption, Biosorption, Absorption or Bioaccumulation: What is the Most Appropriate Term?***

“Adsorption”, “sorption”, “biosorption”, “bio-adsorption”, “absorption” or “bioaccumulation”: What is the 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 clean-up 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 mechanism(s) 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 micro-precipitation, 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. 2013a; 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 co-exist in a biosorption system, and can also function independently.

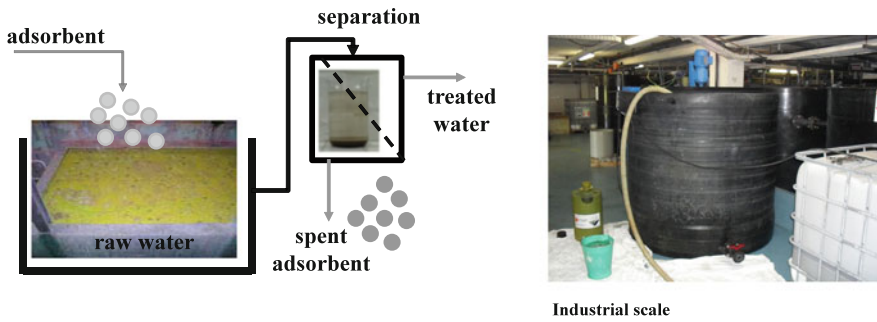
### **2.2.3 Contacting Systems**

When studying adsorption from solutions on materials it is convenient to differentiate between adsorption from dilute solution and adsorption from binary and multi-component mixtures covering the entire range of mole fractions. To judge by the number of papers published annually on adsorption from dilute (single) solution, this subject is more important than adsorption from binary mixtures. It is also 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. 2.2).

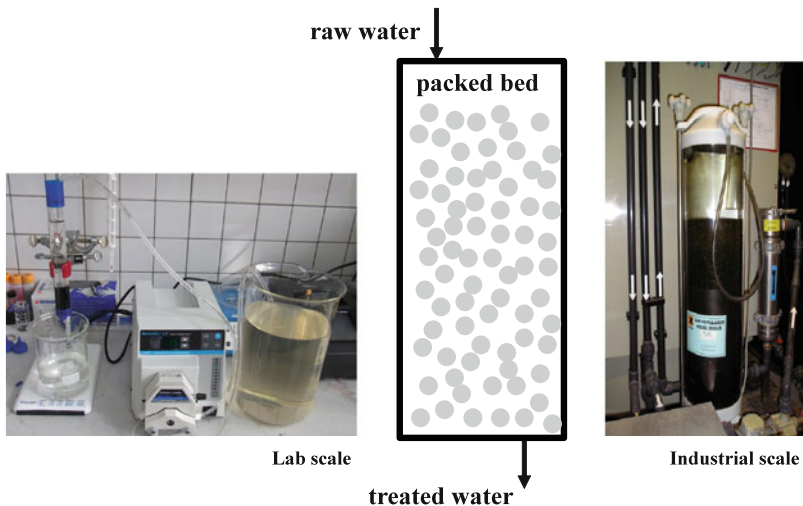
Adsorption processes for decontamination of wastewaters can be carried out either discontinuously in batch reactors or continuously in fixed-bed reactors or columns (Volesky and Holan 1995; Volesky 2001; Crini 2003; Ali 2014). Fixed-bed reactors or dynamic continuous-flow systems are commonly used in 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, temperature, etc. can be controlled and/or adjusted.

## BATCH PROCESS



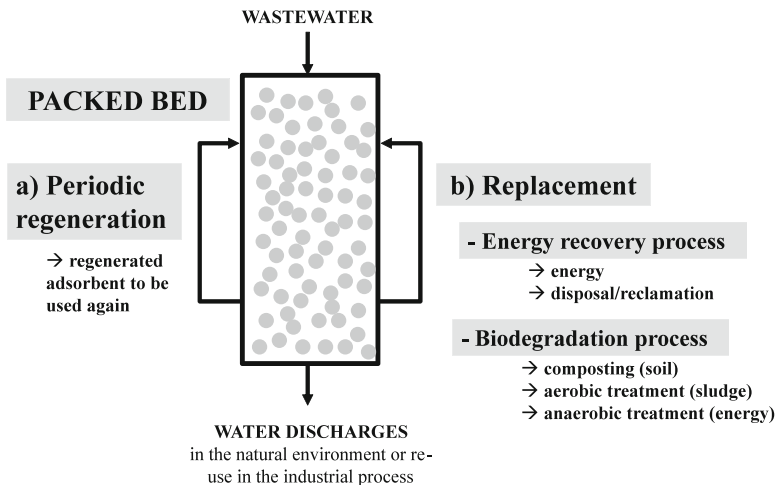
## CONTINUOUS PROCESS



**Fig. 2.2** Schematic representations of two main schemes used for adsorption of pollutants from wastewaters: batch process and continuous process

### ***2.2.4 Desorption of Contaminants***

It is important to point out that adsorption using batch systems is a non-destructive technique involving only a phase change of contaminants, and hence imposes further problems in the form of sludge disposal. For fixed-bed reactors, Fig. 2.3 shows two main strategies (regeneration step or 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



**Fig. 2.3** Schematic representations of two main strategies (regeneration step or replacement) that could be used to deal with spent adsorbent after its usage

opening the possibility of recovering the contaminant extracted from the solution. 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.

### 2.2.5 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: (i) the origin and nature of the solid such as its physical structure (e.g. particle size, specific surface area, porosity), chemical nature and functional groups (e.g. surface charge, pH at the point of zero charge), and mechanical properties; (ii) the activation conditions of the raw solid (e.g. physical treatment, chemical modification); (iii) the influence of process variables used in the contacting system such as contact time, initial pollutant concentration, solid dosage and stirring rate; (iv) the chemistry of the pollutant(s) (for instance, for a dye molecule, its  $pK_a$ , polarity, size and functional groups); and finally, (v) 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).

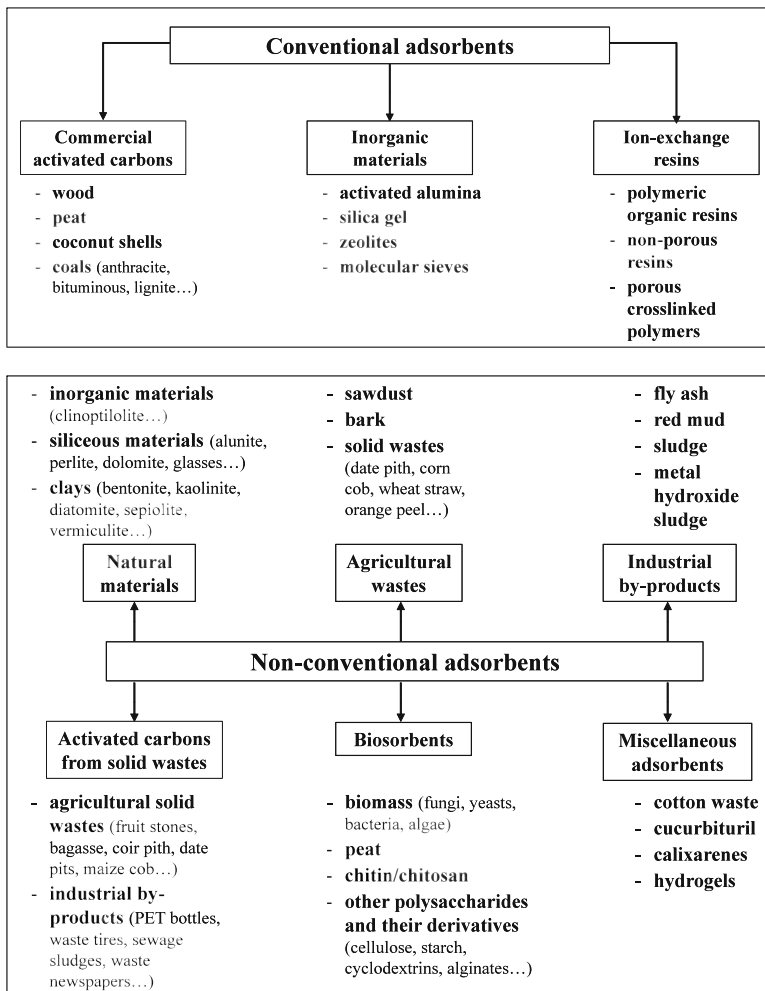
## 2.3 Types of Materials for Contaminant Removal

### 2.3.1 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 shown in Table 2.3. Another simplified classification, introduced by Crini (Crini 2005, 2006; Crini and Badot 2007), can be used as follows: conventional and non-conventional adsorbents. The list of conventional adsorbents includes commercial activated carbons (CAC), commercial ion-exchange resins (polymeric organic resins) and inorganic materials such as commercial activated aluminas (CAA), silica gel, zeolites and molecular sieves

**Table 2.3** Basic types of industrial adsorbents

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



**Fig. 2.4** Conventional and non-conventional adsorbents for the removal of pollutants from waste-waters according to Crini (Crini 2005, 2006; Crini and Badot 2007)

(which are formally not zeolites) (Fig. 2.4). Only four types of generic adsorbents have dominated the commercial use of adsorption: CAC >> zeolites >> silica gel > CAA (Yang 2003). The list of non-conventional adsorbents includes activated carbons (AC) 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. 2.4).

**Table 2.4** Analytical techniques used in adsorption research in order to obtain information on adsorbent characterization, adsorbate characterization and adsorption mechanism

<b>Objective/analytical technique(s)</b>
<b>Characterization of the adsorbent</b>
Elemental composition and distribution: element analysis, energy dispersive X-ray spectroscopy (EDS)
Surface area, porosity (pore size, pore size distribution): nitrogen adsorption (BET measurements)
Crystallographic structure: X-ray diffraction (XRD)
(Surface, inner) morphology: surface electron microscopy (SEM), transmission electron microscopy (TEM), often coupled with EDS
Chemical structure: solid state nuclear magnetic resonance (NMR) spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS)
Ion-exchange capacity: titration
Surface chemistry, surface acid-base characterization: titration, calorimetry, XPS
Surface properties (hydrophilicity, hydrophobicity): contact angle measurements
Determination of the active sites: titration, NMR, Fourier transform infrared spectroscopy (FT-IR), electron spin resonance spectroscopy (ESR)
Swelling capacity: (hypo)osmotic test, pure mechanical swelling
Stability of the material: thermogravimetric analysis (TGA), differential scanning calorimetry (DSC)
<b>Characterization of the adsorbate in the aqueous solution</b>
Determination of the contaminant concentration: atomic absorption spectroscopy (AAS), inductively coupled plasma (ICP), UV-Vis spectrophotometry, fluorescence spectroscopy, photometry (kits tests), ion selective electrode (ISE)
Separation and identification of the contaminant components existing in the solution: liquid chromatography mass spectrometry (LC-MS)
<b>Adsorption mechanism</b>
Chemical characterization of contaminant bound on the material: EDS, NMR, FT-IR
Chemical composition of contaminant bound on the material: XRD
Determination of the oxidation state of contaminant (metal bound): XPS, XAS

### ***2.3.2 Analytical Techniques for the Characterization of an Adsorbent***

Table 2.4 shows examples of analytical techniques used for the characterization of an adsorbent, and more generally available in adsorption research (Crini and Badot 2010; Park et al. 2010; Michalak et al. 2013; Fomina and Gadd 2014; Ramrakhiani et al. 2016). Such techniques often provide distinctive but complementary information not only on the characterization of the adsorbent used but also on adsorption of a target contaminant onto the material and its performance. For example, the characterization of the morphological structure and chemistry of a biomass-based adsorbent used for metal removal is essential for understanding the metal binding mechanism on the biomass surface (Park et al. 2010). This can be elucidated using different techniques such as potentiometric titrations, Fourier transform infrared

spectroscopy (FT-IR), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and also surface electron microscopy (SEM), transmission electron microscopy (TEM). SEM interpretation provides topography of the surface feature and elemental information/metal distribution with a virtually unlimited depth of field. TEM also provides information on the topographical, morphological, compositional and crystalline structures. In general, combination of SEM-EDS and TEM-EDS are performed in order to obtain information regarding the location of the metal. X-ray absorption spectroscopy (XAS) determines the oxidation state of a metal bound to the biosorbent and its coordination environment (Ramrakhiani et al. 2016).

It is well-known that the addition of electrolytes can increase the aggregation of the dye molecules due to reducing the electrical double layer effects to favour self-assembly. For instance, the addition of NaCl in relatively high concentrations can induce the size of the particles in the solution, reducing the space available for dye adsorption (due to occupancy of ions at active sites in competition with dye species), leading to higher aggregation, in accordance with DVLO theory (Blokzijl and Engberts 1993). Liquid chromatography mass spectrometry analysis are useful tools to separate and identify the dye components existing in the solution (Won et al. 2008). Because of their high molar absorptivity, dye molecules and their aggregates are also easily detected by spectrophotometric and photophysical techniques, even at relatively low concentrations. This approach provides information to analyze the type of adsorption mechanisms.

### ***2.3.3 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). Amongst the numerous techniques of contaminant removal, liquid-solid adsorption using AC 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 (CAC) 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, CAC are used as very good adsorbents of organic matter (OM) to reduce the organic load in secondary and/or tertiary treatment, for instance to process heavily polluted effluent (color, COD, TOC) from the textile industry. They are generally very broad spectrum adsorbents that efficiently eliminate man-made pollutants such as pesticides, aromatic and phenolic derivatives (PAH, PCB, etc.), pharmaceuticals, volatile organic compounds (VOC), 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 OM before discharge in the tertiary treatment of industrial effluent. Also, macroporous CAC can be used as supports for bacteria: the bacteria then degrade part of the adsorbed OM (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. CAC biological filters are, for instance, used for the detoxification of effluent loaded with ions (removal of iron, manganese, nitrate) or for the reduction of BOD, COD and TOC (Radovic et al. 2000). An additional major advantage of treatment with CAC 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) CAC 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 CAC have been used for a long time, development is still being pursued particularly as there is increasing demand for very clean water. Research, both fundamental and applied, is currently very active concerning (i) the possible use of new precursors for the CAC such as agricultural and industrial wastes, water bottles made of PET, scrap tyres; (ii) the development of novel classes of materials such as activated carbon cloth, nanotubes; (iii) 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).

AC technology also presents several disadvantages. CAC 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 CAC, 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 (SMEs) cannot employ such treatment due to high cost.



### **2.3.4 Other Commercial Materials**

Various studies have been carried out to replace AC 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; Vijayaraghavan and Yun 2008; Qu 2008; Wan Ngah et al. 2008; Sud et al. 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.

### **2.3.5 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; Gerente 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 byproducts (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). Table 2.5 shows a selection of different reviews on non-conventional adsorbents used for pollutant removal.

**Table 2.5** Selected comprehensively reviews on non-conventional adsorbents used in adsorption-oriented processes (selected references)

Adsorbent	Contaminant(s)	Reference(s)
Agricultural byproducts	Metals, dyes, PAH	Oliveira and Franca (2008), Crini and Badot (2010), Sharma et al. (2011), Nguyen et al. (2013), Rangabhashiyam et al. (2014), Lim and Aris (2014), Kharat (2015), Zhou et al. (2015), Emenike et al. (2016), and Sulyman et al. (2017)
Agri-food wastes	Metals, dyes	Demirbas (2008), Oliveira and Franca (2008), and Kumar et al. (2011)
Fruit and vegetable wastes	Metals, dyes	Swami and Buddhi (2006) and Patel (2012)
Sawdust	Metals, dyes, phenols	Shukla et al. (2002), Swami and Buddhi (2006), Larous and Meniai (2012), Kharat (2015), and Sahmoune and Yeddou (2016)
Bark	Metals, dyes, PAH, chlorinated phenols	Ahmaruzzaman (2008), Demirbas (2008), Kharat (2015), and Sen et al. (2015)
Rice husk	Metals, dyes	Chuah et al. (2005), Ahmaruzzaman (2011), Nguyen et al. (2013), Dhir (2014), and Sulyman et al. (2017)
Wheat	Metals	Ngah and Hanafiah (2008) and Farooq et al. (2010)
Sugar-beet pulp	Metals	Ngah and Hanafiah (2008), Ahmaruzzaman (2011), and Dhir (2014)
Coconut	Metals, phenols	Swami and Buddhi (2006), Bhatnagar et al. (2010), Patel (2012), and Bazrafshan et al. (2016)
<i>Opuntia ficus-indica</i>		Nharingo and Moyo (2016)
Coffee		Anastopoulos et al. (2017a) and Sulyman et al. (2017)
Tea factory waste	Metals	Ahmaruzzaman (2011) and Sulyman et al. (2017)
Peat	Metals, dyes, phosphorus	Brown et al. (2000), Vohla et al. (2011), and Raval et al. (2016)
Lignocellulosic wastes	Metals	Miretzky and Cirelli (2010), Abdolali et al. (2014), and De Quadros Melo et al. (2016)
Cellulose	Metals, dyes, organics	O'Connell et al. (2008), Hubbe et al. (2011), Vandenbossche et al. (2015), and Grishkewich et al. (2017)
Microbial biosorbents	Metals, dyes	Solis et al. (2012), Mudhoo et al. (2012), Ahluwalia and Goyal (2007), and Srivastava et al. (2015)
Bacterial biosorbents	Metals, dyes	Vijayaraghavan and Yun (2008) and Mudhoo et al. (2012)

(continued)

**Table 2.5** (continued)

Adsorbent	Contaminant(s)	Reference(s)
Fungi	Metals, dyes	Kaushik and Malik (2009), Wang and Chen (2009), and Dhankhar and Hooda (2011)
Extracellular polymeric substances	Metals, phosphorus	More et al. (2014) and Li et al. (2015)
Algae, marine algae	Metals, dyes	Brinza et al. (2007), Wang and Chen (2009), Mudhoo et al. (2012), He and Chen (2014), and Zeraatkar et al. (2016)
Plants	Metals, dyes	Ahluwalia and Goyal (2007), Srivastava et al. (2015), and Saba et al. (2016)
Pectins	Metals, dyes	Miretzky and Cirelli (2010), Vandebossche et al. (2015), and Zhao and Zhou (2016)
Starch	Metals, dyes	Crini (2005), Crini and Badot (2010), Panic et al. (2013), Wang et al. (2013), and Vandebossche et al. (2015)
Chitin	Dyes	Yong et al. (2015), Barbusinski et al. (2016), and Anastopoulos et al. (2017b)
Chitosan	Metals, dyes, phenols	No and Meyers (2000), Elwakeel (2010), Li et al. (2008), Crini and Badot (2008), Kyzas et al. (2013b), Liu and Bai (2014), Vakili et al. (2014), Yong et al. (2015), Barbusinski et al. (2016), and Azarova et al. (2016)
Alginate	Metals, dyes	Vandebossche et al. (2015) and Grishkewich et al. (2017)
Cyclodextrins	Metals, dyes, organics	Mocanu et al. (2001), Crini and Morcellet (2002), Crini (2005, 2014), Crini and Badot (2010), Landy et al. (2012a, b), and Panic et al. (2013)
Hydrogels	Metals, dyes, organics	Panic et al. (2013), Khan and Lo (2016), Mittal et al. (2016), Muya et al. (2016), and Grishkewich et al. (2017)
Clays	Metals, dyes	Bhattacharyya and Gupta (2008) and Ngulube et al. (2017)
Industrial byproducts	Metals, dyes	Crini (2005, 2006) and El-Sayed and El-Sayed (2014)
Fly ash	Metals, dyes	Swami and Buddhi (2006), Ahmaruzzaman (2010, 2011), and Raval et al. (2016)
Red mud	Phosphorus, phosphate, fluoride, nitrate, metals, metalloids, dyes, bacteria, virus	Wang et al. (2008) and Ahmaruzzaman (2011)

(continued)

**Table 2.5** (continued)

Adsorbent	Contaminant(s)	Reference(s)
Municipal wastes	Metals, dyes	Bhatnagar and Sillanpää (2010)
Sludge-based adsorbents	Metals, dyes	Raval et al. (2016) and Devi and Saroha (2017)
Nanomaterials	Metals, dyes	Crini and Badot (2010), Ali (2012), Kumar et al. (2014), Zhao and Zhou (2016), and Sadegh et al. (2017)

### 2.3.6 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 byproducts 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; Vandebossche et al. 2015; Khalaf 2016; Morin-Crini and Crini 2017).

In Table 2.6 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 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

**Table 2.6** Principal commercial, conventional and emerging materials for contaminant removal by adsorption and/or ion-exchange processes

Adsorbent	Features/advantages/mechanisms	Limitations/comments
<b>Activated carbons</b>	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
	Versatile material	Performance is dependent on the type of carbon used
	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
Granular activated carbon (GAC)	PAC: used in batch experiments due to low capital cost and lesser contact time requirements	Problems with hydrophilic substances
Other forms	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 (COD, BOD and TOC 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		
<b>Activated carbons from solid wastes</b>	Inexpensive and renewable additional sources of carbon	The performance depends on the raw material, the history of its preparation and treatment conditions
	A potential alternative to existing CAC	Reactivation results in a loss of the carbon

(continued)

**Table 2.6** (continued)

Adsorbent	Features/advantages/mechanisms	Limitations/comments
Agricultural wastes	Interesting properties in terms of surface chemistry, surface charge and pore structure like CAC	Laboratory stage
Wood wastes	Efficient for a large range of pollutants	Identification of adsorption mechanisms
City wastes		
Industrial by-products		
<b>Sand</b>	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)
	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
	Somewhat effective for odor, taste, bacteria and OM	
	Rapid cleaning time	
	Interesting as pretreatment in combination with CAC treatment	
	Physisorption and diffusion mechanisms	
<b>Activated alumina</b>	Relatively well-known and commercially available	Cost of the adsorbent
Bauxite	Highly porous materials with a high surface area and an interesting distribution of both macro and micropores	pH-dependent
	Used mainly as desiccants	Requires a pre-treatment to prevent clogging of the material bed when the water contains SS or to remove certain ions
	Efficient filter for fluoride, selenium and arsenic removal	Fluoride removal: regeneration is often required to make it cost-effective
	Also interesting for the treatment of copper, zinc, mercury, uranium and phosphates	Arsenic removal: needs replacement after four or five regeneration
	Classified by the USEPA as among one of the best available	Can accumulate bacteria

(continued)

**Table 2.6** (continued)

Adsorbent	Features/advantages/mechanisms	Limitations/comments
	technologies for arsenic removal in drinking water	
	The presence of impurities (iron. . .) do not affect the performance	Use of strong acid and base solutions for regeneration step
<b>Zeolites</b>	Easily available and relatively cheap (the price depends on the quality of zeolite)	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)	Requires chemical modification
	Main applications: softening and deionization of water, waste treatment, purification of products	
	Ion-exchange mechanism	
<b>Silica</b>	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)	Requires chemical modification
	Physisorption and chemisorption (ion-exchange) mechanisms	

(continued)

**Table 2.6** (continued)

Adsorbent	Features/advantages/mechanisms	Limitations/comments
<b>Siliceous materials</b>	Abundant, available and low-cost inorganic materials	Important role of the pH of the solution
Alunite	Porous texture with high surface area	Requires physical and chemical modification
Perlite	Regeneration (alunite) 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	
<b>Clays</b>	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	Results are pH-dependent
Fuller's earth	chemical and mechanical stability	Identification of adsorption mechanism (for modified materials)
Sepiolite	Strong candidates for ion-exchange (high cation exchange capacity)	
Kaolinite	Considered as host materials with a strong capacities to adsorb positively charged species; they can also adsorb anionic and neutral species	
Modified materials	Efficient for basic dyes, phenols and metal ions	
	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	
	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		

(continued)



**Table 2.6** (continued)

Adsorbent	Features/advantages/mechanisms	Limitations/comments
<b>Commercial polymeric organic resins and synthetic organic resins</b>	Established treatment process	Derived from petroleum-based raw materials
Porous cross-linked polymers	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, COD 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. . .) 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
Synthetic- or natural-based polymers	Can remove unwanted molecules to lower concentrations than CAC does	Requires a modification for enhanced the water wettability
	No loss of material on regeneration	Non-selective process (conventional resins)
	Organic resins: mechanism due to ion-exchange and/or diffusion into the porous network	Not effective for all dyes (disperse dyes)
	Hydrogels (super-swelling polymers): mechanisms involve both electrostatic interactions and diffusion into the three-dimensional polymeric structures	
<b>Industrial by-products</b>	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	Require physical and chemical modification (red mud)

(continued)

**Table 2.6** (continued)

Adsorbent	Features/advantages/mechanisms	Limitations/comments
	electroplating industry containing insoluble metal hydroxides and salts (calcium, sodium)	
Blast furnace slag and sludge etc.	Red mud: efficient for metalloids and anions removal	Results are pH-dependent (metal hydroxide sludge)
	Ion-exchange mechanism and/or diffusion	Influence of salts (metal hydroxide sludge)
<b>Agricultural solid wastes and byproducts from forest industries</b>	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		
Date pits	Bark: a polyphenol-rich material containing a high tannin content	Results are pH-dependent
Pith	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)
	Possible regeneration (sawdust)	
	Physisorption and chemisorption (ion-exchange, hydrogen bonding) mechanisms	
<b>Biomass</b>	Interesting competitive, cheap and effective technology	Slow process and limiting pH tolerance (algae)
Dead or living biomass	Publicly acceptable	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	Simplicity, versatility, flexibility for a wide range of applications	Results depend on the functional groups present in the biomass
Algae	Availability of different biomasses in large quantities and at low cost	Not appropriate for column systems (an immobilization step is necessary for use in column reactors)
White-rot fungi	Effective and selective adsorbents containing a variety of functional	Technologies are still being developed

(continued)

**Table 2.6** (continued)

Adsorbent	Features/advantages/mechanisms	Limitations/comments
	groups: more selective than traditional ion-exchange resins and CAC	
Yeasts	Important adsorption capacities reported for metal ions and dyes	
Agricultural wastes	Suitable for a wide range of metal concentrations from 100 ppm to 100 ppb or even less (algae)	
Food processing	Fungi can reduce pollutant concentrations to ppb levels	
Aquatic plants	Regeneration is not necessary Physisorption and chemisorption mechanisms	
<b>Peat</b>	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	Requires a pre-treatment or a chemical activation step Influence of some factors (pH, agitation speed, initial dye concentration)
<b>Chitosan</b>	Abundant, renewable, biodegradable and environmentally friendly resource	Nonporous material
Chitin and derivatives	Chitin, the second most abundant natural polysaccharide next to cellulose, is fairly abundant (found in the exoskeleton of shellfish and crustaceans); considered as a byproduct of food processing	Low surface area
Chitosan-based derivatives	Low-cost biopolymer and extremely cost-effective	The performance depends on the origin of the polysaccharide, the

(continued)

**Table 2.6** (continued)

Adsorbent	Features/advantages/mechanisms	Limitations/comments
		degree of N-acetylation and the treatment of the polymer
	Hydrophilic biopolymer with high reactivity and cationic properties in acidic medium	Variability in the polymer characteristics and in the materials used
	Excellent diffusion properties	Not effective for cationic dyes (except after derivatization)
	Versatile materials (powders, gels, beads, fibres. . .) with excellent chelation and complexation behavior	Requires chemical modification to improve both its performance and stability
	Outstanding metal-binding capacities (useful for the recovery of valuable metals) and extremely high affinities for many classes of dyes	Results depend on the functional groups grafted
	High efficiency and selectivity in detoxifying both very dilute or concentrated effluents; a high-quality treated effluent is obtained	Results are strongly pH-dependent
	Easy regeneration if required	Hydrogels: not appropriate for column systems (except for cross-linked beads)
	Physisorption (van der Waals attraction, hydrogen bonding, coulombic attraction) and chemisorption (chelation, complexation) mechanisms	
<b>Miscellaneous adsorbents</b>	Renewable resources (starches, cotton waste, cellulose), economically attractive and feasible	Cost (calixarenes, cucurbiturils, cyclodextrins)
Cellulose	A remarkably high swelling capacity in water	Low mechanical strength
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

(continued)

**Table 2.6** (continued)

Adsorbent	Features/advantages/mechanisms	Limitations/comments
Calixarenes	Cyclodextrins: natural macrocyclic oligomers having a hydrophobic cavity and a amphiphilic character; exhibit high adsorption capacities towards 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	Not appropriate for column systems (hydrodynamic limitations, column fouling, technical constraints)
	Chemisorption mechanism (complexation, inclusion complex formation, ion-exchange)	Requires pre-treatment and/or chemical modification Cucurbituril: dissolution problem

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.

## 2.4 Modeling and Mechanisms of Adsorption

### 2.4.1 Batch Experiments

Batch experiments provide fundamental information on the behavior of the adsorbents used and are thus necessarily carried out in all adsorption studies. Indeed, these methods are widely used to describe the adsorption capacity, the adsorption kinetics and the thermochemistry of the process. The experimental protocol used is simply and easily reproducible. The solution to be treated and the adsorbent are intimately mixed in an agitated contacting reactor/tank for a set time to enable the system to

approach equilibrium, following which the thin slurry is filtered to separate the solid adsorbent and adsorbate from the solution. Batch studies use the fact that the adsorption phenomenon at the solid/liquid interface leads to a change in the concentration of the solution. Adsorption isotherms are then constructed by measuring the concentration of adsorbate in the medium before and after adsorption at a fixed temperature. In this respect, in general, adsorption data including equilibrium and kinetic studies are performed using standard procedures which consist in mixing a fixed volume of contaminant solution, at a known concentration in a tightly closed flask, with a known amount of material (the adsorbent is usually applied in the form of a finely ground powder) in controlled conditions of contact time, agitation rate, temperature, and pH. The solution is stirred on a thermostatic mechanical shaker operating at a constant agitation speed. The solution is then, for example, centrifuged to remove any adsorbent particles, and the supernatant is analyzed for the final contaminant concentration: at predetermined times, the residual concentration is determined by using chemical analysis.

Contaminant concentrations in solution can be estimated quantitatively thanks to a linear regression equation obtained by plotting a calibration curve over a range of concentrations. The amount of contaminant adsorbed (i.e. adsorption capacity, contaminant uptake or abatement) is calculated by subtracting the final solution concentration from the initial value. The results are in general reproducible. Blanks containing no contaminant or adsorbent can be conducted in similar conditions as controls to evaluate possible contaminant change (for example color change in the case of dye molecules) and/or precipitation processes for both components. The amount of contaminant adsorbed at time  $t$  by the material ( $q_t$ ) was obtained from the differences between the concentrations of contaminant added to that in the supernatant.  $q_t$  was calculated from the mass balance equation given by Eq. (2.1) where  $C_o$  and  $C_t$  are the initial and final adsorbate concentrations in liquid phase ( $\text{mg L}^{-1}$ ), respectively,  $V$  is the volume of adsorbate solution (L) and  $m$  the mass of adsorbent used (g). When  $t$  is equal to the equilibrium time (i.e.,  $C_t = C_e$ ,  $q_t = q_e$ ), then the amount of contaminant adsorbed at equilibrium,  $q_e$ , can be calculated by using Eq. (2.2) where  $C_e$  is the liquid phase contaminant concentration at equilibrium ( $\text{mg L}^{-1}$ ). The amount of adsorbate adsorbed can be also expressed as percentage of removal (uptake) or abatement ( $R$  in %) by using Eq. (2.3). The term “abatement”, used by the industrial sector, illustrates the ability of the material to reduce the pollutant load or the concentration of contaminant(s) in effluent to be treated.

$$q_t = \frac{V(C_o - C_t)}{m} \quad (2.1)$$

$$q_e = \frac{V(C_o - C_e)}{m} \quad (2.2)$$

$$R = \frac{100(C_o - C_t)}{C_o} \quad (2.3)$$

## 2.4.2 Modeling

Adsorption properties and equilibrium data, commonly known as adsorption isotherms, describe how pollutants interact with adsorbent materials and so are critical in optimizing the use of adsorbents. In order to optimize the design of an adsorption system to remove contaminant from solutions, it is important to establish the most appropriate correlation for the equilibrium curve. An accurate mathematical description of equilibrium adsorption capacity is indispensable for reliable prediction of adsorption parameters and quantitative comparison behavior for different materials (or for varied experimental conditions) within any given system (Crini and Badot 2007, 2008).

Adsorption equilibrium is established when the amount of contaminant being adsorbed onto the adsorbent is equal to the amount being desorbed (Giles et al. 1958). It is possible to depict the equilibrium adsorption isotherms by plotting the concentration of the contaminant in the solid phase versus that in the liquid phase. The distribution of contaminant molecule (or ion) between the liquid phase and the material is a measure of the position of equilibrium in the adsorption process and can generally be expressed by one or more of a series of isotherm models. The shape of an isotherm may be considered with a view to predicting if an adsorption process is “favorable” or “unfavorable”. The isotherm shape can also provide qualitative information on the nature or the molecule-surface interaction.

There are several isotherm equations available for analyzing experimental data and for describing the equilibrium of adsorption, including the Freundlich, Langmuir, BET, Langmuir-Freundlich, Generalized, Höll-Kirch, Sips, Koble-Corrigan, Radke-Prausnitz, Dubinin-Radushkevich-Kaganer, Redlich-Peterson, Tóth, Temkin, Elovich, Kiselev, Hill-de Boer, Fowler-Guggenheim, Frumkin, Harkins-Jura, Halsey, Nitta, Myers, Henderson, Jossens, Weber-van Vliet, Fritz-Schlunder, and Baudu models (Freundlich 1906; Langmuir 1916, 1918; Radushkevich 1949; Sips 1948; Redlich and Peterson 1959; Dubinin 1960; Toth 1971; Tien 1994; Ho 2003; Allen et al. 2004; Song and Won 2005; Hamdaoui and Naffrechoux 2007a, b; Crini and Badot 2010). The different equation parameters and the underlying thermodynamic assumptions of these models often provide insight into both the adsorption mechanism and the surface properties and affinity of the adsorbent. The two most frequently used equations applied in solid/liquid systems to describe adsorption isotherms are the Langmuir and the Freundlich models and the most popular isotherm theory is the Langmuir type, although these models were initially developed for the modelling of the adsorption of gas solutes onto metallic surfaces (Langmuir 1916, 1918; Polanyi 1920; Dubinin 1966, 1972), and are based on the hypothesis of physical adsorption.

The Langmuir isotherm model is widely used in the literature due to the fact that it incorporates an easily interpretable constant which corresponds to the highest possible adsorbate uptake (i.e. the complete saturation isotherm-curve plateau). The Langmuir equation is represented by Eq. (2.4) where  $x$  is the amount of pollutant adsorbed (mg),  $m$  is the amount of adsorbent used (g),  $C_e$  (mg/L) and  $q_e$  (mg/g) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, respectively, and  $K_L$  (L/g) and  $a_L$  (L/mg) are the Langmuir isotherm constants. The Langmuir isotherm

constants,  $K_L$  and  $a_L$  are evaluated through linearisation of Eq. (2.4). By plotting  $C_e/q_e$  against  $C_e$ , it is possible to obtain the value of  $K_L$  from the intercept which is  $1/K_L$  and the value of  $a_L$  from the slope which is  $a_L/K_L$ . Using these constants, it is also possible to obtain an interesting parameter widely used in the literature to promote a solid material as adsorbent, i.e., the theoretical monolayer capacity of an adsorbent ( $q_{\max}$  in mg/g). Its value, numerically equal to  $K_L/a_L$ , permits to evaluate the maximum adsorption capacity of a material for the adsorption of a target pollutant (Crini 2003, 2005, 2006, 2015). At this stage, it is important to note that the uptake of a contaminant by two material adsorbents must be compared not only at the same equilibrium concentration but also in the same experimental conditions (particularly pH). Another essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor ( $R_L$ , also called equilibrium parameter) which is defined by the Eq. (2.5) where  $C_0$  is the initial concentration (mg/L) and  $a_L$  is the Langmuir constant related to the energy of adsorption (L/mg). The value of  $R_L$  indicates the shape of the isotherms to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ).

$$q_e = \frac{x}{m} = \frac{K_L C_e}{1 + a_L C_e} \quad (2.4)$$

$$R_L = \frac{1}{1 + a_L C_0} \quad (2.5)$$

The Freundlich isotherm is expressed by Eq. (2.6) where  $C_e$  (mg L<sup>-1</sup>) and  $q_e$  (mg g<sup>-1</sup>) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, respectively,  $K_F$  is the Freundlich constant (L<sup>-1</sup> mg) and  $1/n_F$  is the heterogeneity factor. The Freundlich constants are empirical constants which depend on several environmental factors. The value of  $1/n_F$  ranges between 0 and 1, and indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of  $1/n_F$  is equal to unity, the adsorption is linear; if the value is below unity, this implies that the adsorption process is chemical; if the value is above unity, adsorption is a favorable physical process; the more heterogeneous the surface, the closer  $1/n_F$  value is to 0.

$$q_e = K_F C_e^{1/n_F} \quad (2.6)$$

In single-component isotherm studies, the optimization procedure also requires an error function to be defined in order to quantitatively compare the applicability of different models in fitting data. To determine isotherm constants for two-parameter isotherms such as the Langmuir and the Freundlich models, a linear method is available which is based on converting the equation into a linear form by transforming the isotherm variables (Choy et al. 1999; Ho et al. 2000, 2002, 2005; Allen et al. 2003, 2004). Indeed, the typical assessment of the quality of the isotherm fit to the experimental data is based on the magnitude of the correlation coefficient for the regression, i.e. the isotherm giving an  $R^2$  value closest to unity is deemed to provide the best fit. Linearization using such data transformations implicitly alters



the error structure however, and may also violate the error equality of variance (homoscedasticity) and normality hypotheses for standard least squares. This may help to explain earlier observations according to which isotherm parameters derived from the linearized forms of the equations are biased in that the Freundlich parameters produce isotherms which tend to fit the data better at low concentrations whereas those derived for the Langmuir isotherm tend to fit the data better at higher concentrations (Allen et al. 2003; Crini and Badot 2010).

In the literature, linear regression is the most commonly used method to estimate adsorption, and linear coefficients of determination are preferred (Ho et al. 2000, 2005; Allen et al. 2004; Crini and Badot 2010; El-Khaiary 2008; El-Khaiary and Malash 2011). However, the use of this method is limited to solving linear forms of equation which measure the difference between experimental data and theoretical data in linear plots only, but not the errors in isotherm curves. The linearization of a non-linear isotherm expression can produce different outcomes (Allen et al. 2003, 2004; Crini and Badot 2008, 2010). The values of individual isotherm constants can change with the error methodology selected.

As an alternative to the linear transformation, nonlinear optimization has also been applied to determine isotherm parameter values. It most commonly uses algorithms based on the Levenberg-Marquardt or Gauss-Newton methods. The optimization procedure requires an error function to be defined in order to enable the optimization process to determine and evaluate the fit of the isotherm to the experimental equilibrium data (Allen et al. 2003, 2004). Different error functions were proposed such as the sum of the squares of the errors (Eq. 2.7), the hybrid fractional error function (Eq. 2.8), the Marquardt's percent standard deviation (Eq. 2.9), the average relative error (Eq. 2.10) and the sum of the absolute errors (Eq. 2.11). In each case, the isotherm parameters can be determined by minimizing the respective error function across the concentration range studied when using the solver add-in with Microsoft's spreadsheet, Excel.

$$\sum_{i=1}^p (q_{e,calc} - q_{e,meas})_i^2 \quad (2.7)$$

$$\frac{100}{p-n} \sum_{i=1}^p \left[ \frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}} \right]_i \quad (2.8)$$

$$100 \left( \sqrt{\frac{1}{p-n} \sum_{i=1}^p \left[ \frac{(q_{e,meas} - q_{e,calc})^2}{q_{e,meas}} \right]_i} \right) \quad (2.9)$$

$$\frac{100}{p} \sum_{i=1}^p \left| \frac{(q_{e,calc} - q_{e,meas})}{q_{e,meas}} \right|_i \quad (2.10)$$

$$\sum_{i=1}^p |q_{e,calc} - q_{e,meas}|_i \quad (2.11)$$

Several kinetic models can be also used to find the best fitted model for the experimental data obtained (Lagergren 1898; Boyd et al. 1947; Reichenberg 1953; Weber and Morris 1963; Weber et al. 1963; Hall et al. 1966; Blanchard et al. 1984; Treybal 1987; Al-Duri 1996; Ho and McKay 1998, 2003; McKay et al. 1999; Ho 2004, 2006; Azizian 2004; Liu and Liu 2008; Plazinski et al. 2009; Largette and Pasquier 2016). It is well-accepted that there are several steps in a solid-liquid adsorption process: initially the adsorbate molecules/ions migrate from the bulk of the solution to the material surface (bulk diffusion); the molecules diffuse through the boundary layer to the surface of the material (film diffusion); then, the adsorbate diffuses from the surface to the interior of the particle (pore diffusion, intraparticle diffusion); and finally the molecules reacts with the active sites on the surface of the material (physical adsorption, chemical reaction).

The use of kinetic models such as diffusional models and adsorption models permit elucidation of the adsorption mechanism. The diffusional models assume that the diffusion is the rate limiting step. They are divided in two groups (Crini and Badot 2010). The first is the external mass transfer model which assume that the transfer is controlled by boundary layer diffusion (e.g. Boyd's film-diffusion equation, Spahn and Schlunder model). The adsorbate molecules must pass through the hydrodynamic layer to the surface of the material. Transportation through the boundary layer is due to molecular diffusion, and the distance the adsorbate must travel, or the thickness of the boundary layer, depends on the velocity of the bulk solution. The size of the boundary layer affects the rate of transportation (the thinner the boundary layer, the higher the rate of the transportation). The second gathers the internal diffusion models suggesting a mass transfer through the pores (e.g. Crank model, Weber and Morris model, Bangham model). The internal transport occurs after the adsorbate has passed through the boundary layer and must be transported through the pores to adsorption sites. This intraparticle transportation may occur by molecular diffusion through the solution in the pores (pore diffusion) or by diffusion along the material surface (surface diffusion) after adsorption takes places. The final step, adsorption, is the attachment of the adsorbate onto the material surface at available sites. This step is very rapid, and therefore one of the preceding diffusion steps will control the rate of mass transfer.

In the adsorption models, the adsorption is considered to be the slowest process. This is the case when the adsorbate uptake on the material is of chemical nature. These models include the pseudo-first order model (Lagergren model), the pseudo-second order model (Ho and McKay equations), the pseudo-n order model (for n different from zero), the Langmuir model, and the Elovich equation. The two most popular kinetic equations are pseudo-second-order kinetic and intraparticle diffusion equations proposed by Ho and McKay, and Weber and Morris, respectively.

The pseudo-second order model can be represented in the linear form described by Eq. (2.12) where  $q_t$  (mg/g) and  $q_e$  (mg/g) are the amount of pollutant adsorbed at time  $t$  and equilibrium, respectively, and  $k_2$  is the equilibrium rate constant of pseudo-second order adsorption (g/mg min). The parameters  $k_2$  and  $q_e$  can be directly obtained from the intercept and slope of the plot of  $t/q_t$  against  $t$ . This model is commonly used to describe kinetics of contaminant adsorption on solid

adsorbents, although as pointed out by McKay's group (Ho and McKay 1998; McKay et al. 1999), the application of a single kinetic model to the adsorption on materials may be questionable because of the heterogeneity of the adsorbent surfaces and diversity of adsorption phenomena (i.e. transport, diffusion, reactions). Such approach has no physical significance and it is more reasonable to interpret the kinetic data in term of mass transfer.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2.12)$$

In a batch system under rapid stirring, there is a possibility that the transport of the adsorbate from the solution into the bulk of the adsorbent is the rate controlling step. This possibility was tested in terms of a graphical relationship between the amount of pollutant adsorbed and the square root of time. According to the intraparticle diffusion model proposed by Weber and Morris, the initial rate of intraparticle diffusion is given by the Eq. (2.13) where  $q_t$  is the amount of pollutant on the surface of the sorbent at time  $t$  (mg/g),  $k_i$  is the intraparticle diffusion rate constant (mg/g min<sup>1/2</sup>),  $t$  is the time (min) and  $C$  is the intercept (mg/g). According to Eq. (2.13), a plot of  $q_t$  versus  $t^{1/2}$  should be a straight line when adsorption mechanism follows the intraparticle diffusion process. In general, the plots present a multi-linearity, which indicates that two or more steps occur in the process.

$$q_t = k_i t^{1/2} + C \quad (2.13)$$

Finally, the adsorption characteristics of a material can be expressed in thermodynamic parameters such as  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  (entropy change). These parameters can be calculated by using the thermodynamic equilibrium coefficient obtained at different temperatures and concentrations. The models of Arrhenius, Gibbs, van't Hoff and Clausius-Clapeyron can be used (Crini and Badot 2008). The values of  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  provide valuable information about the thermodynamics of the adsorption process.  $\Delta G$  addresses the possibility and feasibility of a certain reaction. Its negative value shows the process is feasible and spontaneous.  $\Delta H$  shows the route of energy in the process and its positive value indicates an endothermic system. Some authors conclude that the nature of the contaminant adsorption is predominantly physical, involving weak interactions.  $\Delta S$  can be used to describe the randomness at the solid/solution interface during the adsorption process.

There is no doubt that mathematical modeling is an invaluable tool for the analysis and design of adsorption systems and also for the theoretical evaluation and interpretation of thermodynamic parameters (Allen et al. 2004). However, two important points must be pointed out. The first is that, although these adsorption and kinetic models remain a useful and convenient tool for the comparing results from different sources due to their highly idealistic simplicity, a given plot is an empirically relationship (Liu and Liu 2008; Liu and Wang 2008; Lin and Wang 2008; Wu et al. 2009; Rudzinski and Plazinski 2009; Douven et al. 2015). An isotherm may fit experimental data accurately under one set of conditions but fail entirely under

another. No single model has been found to be generally applicable. This is readily understandable in the light of the hypotheses associated with their respective deviations. In addition, the two-parameter isotherm model such as the Langmuir and the Freundlich models are based on the hypothesis of physical adsorption. In the case of dye adsorption onto a biosorbent, which is more chemical than physical, it would be more appropriate to consider pollutant adsorption with models based on chemical reactions. However, these models are complicated in nature. Simple kinetic models used in the literature are also questionable because, generally speaking, these models cannot represent the real course of adsorption and thus cannot offer useful information to gain insight in mechanism. It is more reasonable to interpret the kinetic data in term of mass transfer (homogeneous diffusion model, double exponential model, etc.) but these models are also complex and effective graphical analysis software are required to solve mathematical models. The book published by Tien (1994) can be consulted on this topic. The second point is related the abundant literature data. Despite the number of papers published, there is as yet little literature containing a full study comparing various models and this topic clearly needs further detailed research (Wase and Forster 1997; McKay 1999; Cooney 1999; Yang 2003; Hamdaoui and Naffrechoux 2007a, b; Crini and Badot 2007, 2010).

### 2.4.3 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 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).

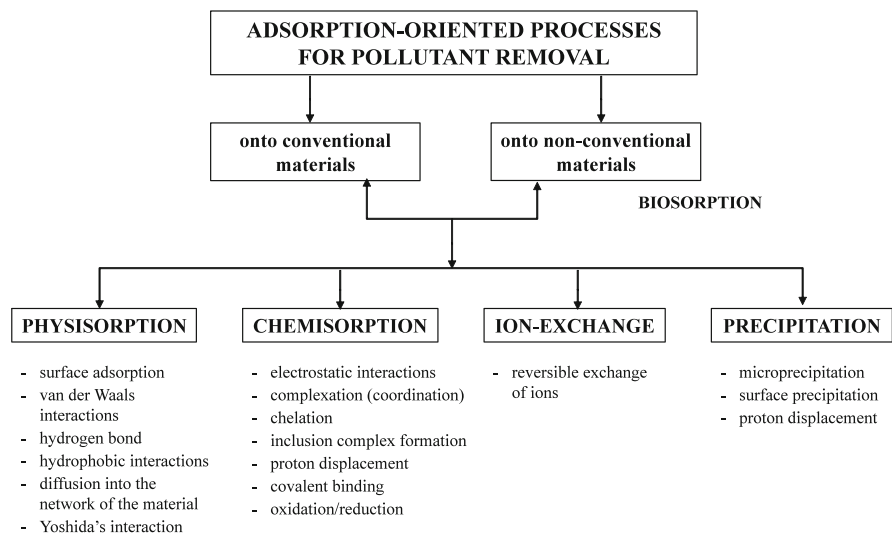
Despite the large number of papers devoted to the adsorption of contaminants onto conventional or non-conventional adsorbents, most focus on the evaluation of adsorption performances and only a few aim at gaining a better understanding of adsorption mechanisms (Veglio' and Beolchini 1997; Crini 2005). 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 ( $\pi$ - $\pi$  interactions, Yoshida's interactions)
- oxidation/reduction
- inclusion complex formation
- diffusion into the network of the material
- 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. 2.5 (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



**Fig. 2.5** Classification of pollutant adsorption mechanisms according to Crini (Crini 2005, 2006; Crini and Badot 2007)

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).

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; Dubinin 1966; Radovic et al. 2000; Pereira et al. 2003).

For biosorbents, the adsorption mechanism are 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 decolourisation 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. (2017) 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 to 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).

## 2.5 Concluding Remarks

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 centre 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.

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