Utilization of Absorption Process for the Removal of Emerging Contaminants from Water and Wastewater

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Abstract: Emerging contaminants are chemicals recently discovered in natural streams as a result of human and industrial activities. Most of them have no regulatory standard and can potentially cause deleterious effects in aquatic life at environmentally relevant concentrations. The conventional wastewater treatment plants (WWTPs) are not always effective for the removal of these huge classes of pollutants and so further water treatments are necessary. This chapter has the aim to study the absorption process in the removal of emerging compounds. Firstly, a brief description of absorption mechanism is given and then the study of conventional and non-conventional absorbents for the removal of emerging compounds is reviewed with the comparison between them.

Keywords: Low-cost absorbents, Conventional absorbents, Pharmaceuticals

Introduction: Since the end of the last century a large amount of products, such as medicines, disinfectants, contrast media, laundry detergents, surfactants, pesticides, dyes, paints, preservatives, food additives, and personal care products, have been released by chemical and pharmaceutical industries threatening the environment and human health. Currently there is a growing awareness of the impact of these contaminants on groundwater, rivers, and lakes. Therefore the removal of emerging contaminants of concern is now as ever important in the production of safe drinking water and the environmentally responsible release of wastewater [1, 2]. Although very little investment has been made in the past on water treatment facilities, typically water supply and treatment often received more priority than wastewater collection and treatment. However, due to the trends in urban development along with rapid population increase, wastewater treatment deserves greater emphasis. Several research studies showed that, treated wastewater, if appropriately managed, is viewed as a major component of the water resources supply to meet the needs of a growing economy. The greatest challenge in implementing this strategy is the adoption of low cost wastewater treatment technologies that will maximize the efficiency of utilizing limited water resources and ensuring compliance with all health and safety standards regarding reuse of treated wastewater effluents. Treatment options which are typically considered for the removal of emerging contaminants from drinking water as well as wastewater include absorption, Advanced Oxidation Processes (AOPs), Nano filtration (NF), and Reverse Osmosis (RO) membranes [3, 4]. However, the shortcomings of most of these methods are high investment and maintenance costs, secondary pollution (generation of toxic sludge, etc.) and complicated procedure involved in the treatment. On the other hand physicochemical treatments such as coagulation/ flocculation processes were generally found to be unable to remove Endocrine Disrupting Compounds (EDCs) and Pharmaceuticals and Personal Care Products (PPCPs). Although AOPs can be effective for the removal of emerging compounds, these processes can lead to the formation of oxidation intermediates that are mostly unknown at this point. Conversely adsorption processes do not add undesirable by-products and have been found to be superior to other techniques for wastewater treatment in terms of simplicity of design and operation, and insensitivity of toxic substances [5]. Among several materials used as adsorbents, Activated Carbons (ACs) have been used for the removal of different types of emerging compounds in general but their use is sometimes restricted due to high cost. Furthermore when AC has been exhausted, it can be regenerated for further use but regeneration process results in a loss of carbon and the regenerated product may have a slightly lower absorption capacity in comparison with the virgin-activated carbon. This has resulted in attempts by various workers to prepare low cost alternative adsorbents which may replace activated carbons in pollution control through absorption process and to overcome their economic disadvantages [6]. 16 M. Grassi et al. Recently natural materials that are available in large quantities from agricultural operations have been evaluated as low cost absorbents and environmental friendly [7]. Moreover the utilization of these waste materials as such directly or after some minor treatment as absorbents is becoming vital concern because they represent unused resources and cause serious disposal problems [8–11]. A growing number of studies have been carried out in recent years to evaluate the behavior of emerging absorbents such as agricultural products and by-product for emerging contaminants removal. On the other hand industrial wastes, such as, fly ash, blast furnace slag and sludge, black liquor lignin, red mud, and waste slurry are currently being investigated as potential absorbents for the removal of the emerging contaminants from wastewater. This chapter presents the state of art of wastewater treatment by absorption focusing in special way on removal of emerging contaminants. A brief introduction of the process is first given and then the use of commercial (activated carbons, clay and minerals) and unconventional absorbents (agricultural and industrial waste) is discussed, taking into account several criteria such as absorption capacities (qe), equilibrium time (te) and emerging contaminant removal efficiency, which make them more or less suitable to be considered green.

Absorption Process

Mechanisms and Definitions: Absorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid– solid interface. The substance being adsorbed is the absorbate and the absorbing material is termed the adsorbent. The properties of absorbates and absorbents are quite specific and depend upon their constituents. The constituents of absorbents are mainly responsible for the removal of any particular pollutants from wastewater [7]. If the interaction between the solid surface and the adsorbed molecules has a physical nature, the process is called physisorption. In this case, the attraction interactions are van der Waals forces and, as they are weak the process results are reversible. Furthermore, it occurs lower or close to the critical temperature of the absorbed substance. On the other hand, if the attraction forces between absorbed molecules and the solid surface are due to chemical bonding, the absorption process is called chemisorptions. Contrary to physisorption, chemisorptions occurs only as a monolayer and, furthermore, substances chemisorbed on solid surface are hardly removed because of stronger forces at stake. Under favorable conditions, both processes can occur simultaneously or alternatively. Physical absorption is accompanied by a decrease in free energy and entropy of the absorption system and, thereby, this process is exothermic.

Absorption Isotherms: In a solid–liquid system absorption results in the removal of solutes from solution and their accumulation at solid surface. The solute remaining in the solution reaches a dynamic equilibrium with that absorbed on the solid phase. The amount of absorbate that can be taken up by an adsorbent as a function of both temperature and concentration of absorbate, and the process, at constant temperature, can be described by an absorption isotherm according to the general Eq. (2.1): qt ¼

ðC0 _ CtÞV
m
ð2:1Þ

where qt (mg/g) is the amount of absorbate per mass unit of adsorbent at time t, C0 and Ct (mg/L) are the initial and at time t concentration of absorbate, respectively, V is the volume of the solution (L), and m is the mass of adsorbent (g). Taking into account that absorption process can be more complex, several absorption isotherms were proposed. Among these the most used models to describe the process in water and wastewater applications were developed by (i) Langmuir, (ii) Brunauer, Emmet, and Teller (BET), and (iii) Freundlich. The Langmuir absorption model is valid for single-layer absorption, whereas the BET model represents isotherms reflecting apparent multilayer absorption. So, when the limit of absorption is a monolayer, the BET isotherms reduce to the Langmuir equation. Both equations are limited by the assumption of uniform energies of absorption on the surface.

The Langmuir isotherm is described by the Eq. (2.2): qe

qm¼
bCe
1 þ bCe
ð2:2Þ

where qe (mg/g) is the amount of absorbate per mass unit of adsorbent at equilibrium, Ce is the liquid-phase concentration of the absorbate at equilibrium (mg/L), qm is the maximum absorption capacity (mg/g) and b is the Langmuir constant related to the energy of absorption (L/mg). With the additional assumption that layers beyond the first have equal energies of absorption, the BET equation takes the following simplified form: q#e_q#m ¼ _BC#e____C#S _ C_½1 þ ðB _ 1Þ_C#e__C#S___ ð2:3Þ in which CS is the saturation concentration of the solute, B is a constant which takes into account the energy of interaction with the surface, and all other symbols have the same significance as in Eq. (2.2).

The data related to absorption from the liquid phase are fitted better by Freundlich isotherm equation [12]. It is a special case for heterogeneous surface energies. Freundlich isotherm is described by the Eq. (2.3): qe ¼ KFC1=n

e ð2:4Þ
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where KF (mg/g) (L/mg)1/n is the Freundlich capacity factor and 1/n is the Freundlich intensity parameter. The constants in the Freundlich isotherm can be determined by plotting log qe versus log Ce.

Factors Affecting Absorption: The factors affecting the absorption process are: (i) surface area, (ii) nature and initial concentration of absorbate, (iii) solution pH, (iv) temperature, (v) interfering substances, and (vi) nature and dose of absorbent.

Since absorption is a surface phenomenon, the extent of absorption is proportional to the specific surface area which is defined as that portion of the total surface area that is available for absorption [13, 14]. Thus more finely divided and more porous is the solid greater is the amount of absorption accomplished per unit weight of a solid absorbent [15]. The major contribution to surface area is located in the pores of molecular dimensions. For example, the surface area of several activated carbon used for wastewater treatment is about 1,000 m2/g, with a mean particle diameter of about 1.6 mm and density of 1.4 g/cm3. Assuming spherical particles, only about 0.0003% of the total surface is the external surface of the carbon particle [16]. The physicochemical nature of the absorbent drastically affects both rate and capacity of absorption. The solubility of the solute greatly influences the absorption equilibrium. In general, an inverse relationship can be expected between the extent of absorption of a solute and its solubility in the solvent where the absorption takes place. Molecular size is also relevant as it relates to the rate of uptake of organic solutes through the porous of the absorbent material if the rate is controlled by intraparticle transport. In this case the reaction will generally proceed more rapidly with decrease of absorbate molecule [15, 17–19]. The pH of the solution affects the extent of absorption because the distribution of surface charge of the absorbent can change (because of the composition of raw materials and the technique of activation) thus varying the extent of absorption according to the absorbate functional groups [15, 20–22]. For example Hamdaoui [23] showed that absorption of methylene blue on sawdust and crushed brick increased by increasing pH (until a value of 9). For pH lower than 5 both absorbents were positively charged: in this case, the absorption decreased because methylene blue is a cationic dye. Another important parameter is the temperature. Absorption reactions are normally exothermic; thus the extent of absorption generally increases with decreasing temperature [15, 24–26]. Finally, the absorption can be affected by the concentration of organic and inorganic compounds. The absorption process is strongly influenced by a mixture of many compounds which are tipically present in water and wastewater. The compounds can mutually enhance absorption, may act relatively independently, or 2 Removal of Emerging Contaminants from Water and Wastewater 19 may interfere with one other. In most cases, as also shown hereinafter, natural organic matter (NOM) negatively affects the absorption of emerging compounds in surface waters and wastewaters [22, 27, 28].

Removal of Emerging Compounds by Absorption: Emerging contaminants are defined as compounds that are still unregulated or in process of regularization and that can be a threat to environmental ecosystems and human health [29, 30]. The words ‘‘emerging compounds’’ encompass a huge quantity of pollutants, including PPCPs, synthetically and naturally occurring hormones, industrial and household chemicals, nano materials, and some disinfection by-products (DBPs), as well as their transformation products [30]. Sources and pathways of emerging compounds into the environment depend on how (and where) they are used and how the products containing them are disposed. Figure 2.1 shows the possible contamination pathways of emerging contaminants. The most of emerging compounds are sent to conventional Wastewater Treatment Plants (WWTPs) that allow only partial removal of micro pollutants by stripping, sorption, and biological degradation. Stripping is negligible compared with the other ones because most of emerging compounds are characterized by low volatility property. It has been demonstrated that stripping efficiency is not relevant even for musk fragrances which are slightly volatile with an Henry constant (H) value about of 0.005 [31, 32]. Sorption on primary and secondary sludge is more important than stripping process. It occurs like absorption on the lipid fraction of the sludge, especially on the primary sludge, and absorption onto sludge through electrostatic interactions between positively charged compounds and negatively charged microorganisms surface [32]. So acid and lipophilic compounds (e.g. hormones, anti-inflammatories, fluoroquinolones) are efficiently removed in WWTPs unlike basic (clofibric acid, bezafibrate), neutral (diazepam, phenazone, and carbamazepine), and polar compounds (beta-lactam antibiotics) [33, 34].

In addition to chemical properties of specific compounds, WWTPs operating conditions are also important to study the absorption onto sludge of emerging compounds. For example, ciprofloxacin, a polar compound, sorbed very well onto suspended solids [34], while diclofenac, which is an acid drug, is characterized from a strong variability in the removal percentage (15–80%) because of different WWTPs conditions [33, 35]. Another mechanism removal is biological degradation which is described by reaction rate constant kbiol. According to this parameter, compounds can be classified in [31, 32]:

- Highly biodegradable kbiol[10 L/gSS d;
- Moderately biodegradable 0.1\kbiol\10 L/gSS d;
- Hardly biodegradable kbiol\0.1 L/gSS d. 20 M. Grassi et al.

Also in this case biological operating conditions are of relevant importance. Indeed, biological decomposition increases with the age of sludge [31, 34] and hydraulic retention time [36]. Some compounds are removed with low sludge age (2–5 days), other ones are hardly degradable also with sludge age greater than 20 days [34]. So, in many cases, WWTPs do not have right operating conditions to remove well-defined emerging compounds. This implies the upgrading of the plant or the use of a tertiary treatment to avoid the input of pollutants into the environment. In the last years many studies were carried out to remove emerging pollutants by absorption process. The most used absorbents were commercial ones (such as natural clays, minerals, and activated carbons).

Commercial Absorbents

Activated Carbon: Activated carbon prepared from different source materials (e.g. coal, coconut shells, lignite, wood, etc.) is the most popular and widely used absorbent in wastewater treatment throughout the world. Its application in the form of Fig. 2.1 Potential sources and pathways of emerging compounds into the environment 2 Removal of Emerging Contaminants from Water and Wastewater 21 carbonized wood (charcoal) has been described first in the Sanskrit medical lore and then in the Egyptian papyrus. Sanskrit writings, dating about 2,000 BC, tell how to purify impure water by boiling it in copper vessels, exposure to sunlight, and filtering through charcoal [6]. Activated carbon is produced by a process consisting of pyrolysis of raw material followed by activation with oxidizing gases. The product obtained is known as activated carbon and generally has a very porous structure with a large surface area ranging from 600 to 2,000 m2/g. Most studies concerning the removal of micropollutants in aqueous solution by absorption are carried out by using activated carbon. However, with the aim of implementing the technology at full scale application, studies of water and wastewater are most significant. For this reason in this section only works concerning emerging contaminants found in drinking water and in wastewater will be discussed. Redding et al. [37] evaluated the efficiency of rapid small-scale column for the treatment of a lake water spiked with 29 EDCs and PPCPs with concentration values of 100–200 ng/L. Authors studied the behavior of two kinds of carbons: a conventional activated carbon and two modified lignite carbons prepared utilizing a high-temperature steam and methane/steam. The conventional one showed a shorter bed life than modified lignite carbons. Indeed lignite variants removed EDCs/PPCPs 3–4 times longer than did commercial carbon. Furthermore the most absorbed compounds were steroids (androstenedione, estradiol, estriol, estrone, ethynylestradiol, progesterone, and testosterone) which are characterized by quite similar molecular volume, which averaged 80 mL/mol.

The removal of 17b-estradiol from a raw drinking water was studied from Yoon et al. [22] using 5 mg/L of PAC (coal-based). The removal percentage was[90% regardless contact times and at a very low pollutant concentration (27 ng/L). This compound was also studied in the work of Yoon et al. [17]. In this study two raw drinking waters were spiked with three contaminants: 17b-estradiol, 17a-ethynylestradiol, and bisphenol A. They were removed by absorption on several different PAC coal-based except a wood-based one. After 1 h contact time and 45 mg/L of PAC the removal was 99% for all compounds. Increasing contact time (4 and 24 h) PAC doses were reduced (15 and 9 mg/L respectively). It is evident that contact time and absorbent dose are important parameters in the absorption process [28, 38]: a right combination of each allows to reach the right operating conditions in a full-scale plant. Another important parameter is water-octanol partition coefficient (log Kow). In particular, depending on log Kow, hydrophobic pollutants [4) have higher absorption capacity [39–41], also if this is not always true [42, 43]. For example, Westerhoff et al. [42] evaluated the removal of 62 different EDCs/PPCPs (10–250 ng/L) in three drinking water sources. Results showed a relation between percentage EDCs/PPCPs removal and log Kow, but not for all compounds (e.g. caffeine, pentoxyfilline).

As previously said, another parameter which can negatively affect absorption process is NOM, which competes with the specific compounds for absorption sites. It is obvious that the presence of organic matter can block pores of activated carbon and, for this reason, the removal percentage decreases if compared with results of tests carried out on model water [18, 22, 28, 44]. The problem of organic materials in water gets worse for wastewater treatment and greater carbon doses or a combination of different treatments are needed to reach a good removal percentage and to control the problem of fast deterioration of absorbents. For instance, Hartig et al. [45] investigated the removal by PAC absorption of two micropollutants (N–n-butylbenzenesulphonamide and sulphamethoxazole) from tertiary wastewater effluents prior to and after filtration with a tight ultrafiltration membrane. The results showed that membrane filtration prior to PAC absorption may lead to improved elimination rates for adsorbable and low molecular weight micropollutants. Another example was reported by Baumgarten et al. [46] who examined the removal of floxacins and their precursors present in wastewater by a combination of membrane biological reactor (MBR) with PAC absorption. PAC addition into wastewater of MBR pilot plant significantly improved removal rates (floxacins[95% and fluoroquinolonic acid as high as 77% removals at 50 mg/L initial PAC dose). Furthermore, PAC absorption process was used to treat the permeate of MBR plant. In this case two kinds of PACs were used. The best absorbent allowed to reach removal percentages [70% with a PAC dose of 50 mg/L. Increasing PAC dose up to 500 mg/L, a nearly complete elimination of fluoroquinolonic acids and floxacins was achieved. The removal of micropollutants from wastewater was also carried out by the addition of commercial PAC directly to the activated sludge system with and without the absorbent recycling to biological process [47]. Results showed that the Fig. 2.2 Removal percentages correspond to 1 mg/l dose ofactivated carbon CC-AC, 100 mg/l dose of Z1 and Z2 and three weeks contact time, 5 mg/l dose of PAC and 4 h contact time. Amended from Ref. [4] with kind permission of _ Elsevier (2009) 2 Removal of Emerging Contaminants from Water and Wastewater 23 removal efficiency increased from 30 to 50% with PAC (10 mg/L) recycling into the biological tank. Increasing PAC concentration to 15 mg/L and with PAC recycling all compounds were removed by more than 80%.

Clays: Natural clay minerals are well known from the earliest day of civilization. Because of their low cost, high surface area, high porosity, and abundance in most continents, clays are good candidates as absorbents. There are many kinds of clay: smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite, sepiolite, bentonite, kaolinite, diatomite, and Fuller's earth (attapulgite and montmorillonite varieties) [6]. The absorption capacities depend on negative charge on the surface, which gives clay the capability to adsorb positively charged species. Putra et al. [21] investigated the removal of amoxicillin from aqueous solutions by absorption on bentonite. A quite high value of initial amoxicillin concentration (300 mg/L) was chosen to represent pharmaceutical wastewater. Absorption of amoxicillin was strongly affected by pH because it can alter the charge of amoxicillin molecule. In particular, qe values increased as the pH value decreased. In this study, absorption capacity of bentonite was compared with a commercial GAC. Both absorbents were found to be quite effective because removal percentage as high as 88% was achieved. qe value was comparable (around 20 mg/g or bentonite and 25 mg/g for commercial activated carbon), but absorption equilibrium time for activated carbon was only 35 min compared to 8 h of bentonite. The main reason could be the different surface area of the two absorbents: 92 m2/g for bentonite and 1,093 m2/g for GAC. Bekçi et al. [24, 48] investigated montmorillonite as absorbent in the removal of trimethoprim, one of the main antibacterial agents used in human and veterinary medicine worldwide. Results showed that the process was exothermic because of absorption efficiency increased as temperature decreased. As a consequence of thermodynamic studies, the authors demonstrated that physisorption was the main mechanism of absorption. Another parameter that affected absorption of trimethoprim was pH. At low pH conditions (in an aqueous solution montmorillonite has a pH value of 3.31), trimethoprim is in the protonated form, so it was strongly absorbed to the negatively charged surface of the montmorillonite. In the best conditions, the amount of drug absorbed was 60 mg/g for 1 h of contact time (initial compound concentration was 290.3 mg/L).

Minerals: Another class of absorbents includes natural minerals. Among these zeolite and goethite have been investigated in the absorption of pharmaceuticals. Zeolite is 24 M. Grassi et al. typically used for the removal of dyes and heavy metals. Like clay minerals, absorption capacity is linked to negative charge on the structure. Ötker and Akmehmet-Balciog˘lu [26] investigated the absorption of enrofloxacin, a fluoroquinolone group antibiotic, onto natural zeolite and subsequent absorbent regeneration by ozone treatment. The best results were achieved for lower pH values (pH investigated values were 5, 7, and 10) because of enrofloxacin is in the cationic form and so the absorption onto negatively charged zeolite surface was better. Unlike absorption clays, the process was endothermic, with higher enrofloxacin removal at higher investigated temperature. However, the results obtained with varying temperature (28, 37, 45, and 50 _C) showed a little change in the absorbed amount, ranging from 16 to 18 mg/g. Absorption equilibrium was reached at 200 min and the absorbed amount at equilibrium was about 18 mg/g. The regeneration process by ozone oxidation (1.4 g/h) was able to decompose enrofloxacin absorbed onto zeolite as well as to affect zeolite pore structure by decreasing pore size. Really interesting is the study of Rossner et al. [4] concerning a lake water spiked by a mixture of 25 emerging contaminants at varying concentration (200–900 ng/L). The absorbents used were one coconut-shell-based GAC (CC-AC), one carbonaceous resin and two high-silica zeolites, Z1 (modernite zeolite) and Z2 (Y zeolite). The order of process efficiency was activated carbon [carbonaceous resins [zeolites. Carbonaceous absorbents were more effective for micropollutants removal probably because activated carbons exhibit a broader micropore size distribution, in which compounds of different shapes and sizes can be effectively accommodated. High-silica zeolites, on the contrary, have uniform pore sizes, which is effective for the removal of a specific compound but not for a broad mixture of contaminants. In Fig. 2.2 results were compared with the average removal percentages obtained in four natural waters treated with 5 mg/L of powdered activated carbon (PAC) [42]. Removal values obtained with CC-AC and PAC were comparable also if the brand and the concentration of two absorbents were different. Z1 allowed to reach high removal percentage of micropollutants but not for all compounds such
as activated carbons. Z2 was the worst absorbent and removal values were really different from Z1 (only fluoxetine, oxybenzone and triclosan were removed by Z2). Zhang and Huang [19] investigated the removal of seven fluoroquinolones (FQs) and five structurally related model amines with Fe oxides, using two sources of goethite, with a focus on both absorption and oxidation by Fe oxides. The authors found out that flumequine

can be absorbed more strongly to goethite than other FQs, due to effects of speciation and molecular size. Under investigated conditions (pH 5), absorbent was positively charged, flumequine in neutral form,
and the other FQs in cationic form, thus explaining the lower absorption for the latter. Furthermore, in terms of molecular size, the other FQs being characterized 2 Removal of Emerging Contaminants from Water and Wastewater 25 by a larger molecule structure than flumequine may obstruct absorption active sites.

Low Cost Absorbents: Although, activated carbon is undoubtedly considered as universal absorbent for the removal of diverse kinds of pollutants from water, its widespread use is sometimes restricted due to the high costs [8, 9, 49]. Attempts have been made to develop low-cost alternative absorbents which may be classified in two ways (Fig. 2.3) either (i) on basis of their availability, i.e., (a) natural materials (wood, peat, coal, lignite etc.), (b) industrial/agricultural/domestic wastes or by-products (slag, sludge, fly ash, bagasse flyash, red mud etc.), and (c) synthesized products; or (ii) depending on their nature, i.e., (a) inorganic and (b) organic material [6, 8, 10, 11].

Agricultural Waste: The basic components of the agricultural waste materials include hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch, containing a variety of functional groups [10]. In particular agricultural materials containing cellulose show a potential sorption capacity for various pollutants. If these wastes could be used as low-cost absorbents, it will provide a two-fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly the low-cost absorbent, if developed, can reduce the treatment of wastewaters at a reasonable cost [9, 50]. Agricultural waste is a rich source for activated carbon production due to its low ash content and reasonable hardness [51]. The agricultural solid wastes from cheap and readily available resources such as almond shell, hazelnut shell, poplar, walnut sawdust [52], orange peel [53, 54], sawdust [55], rice husk [56], sugarcane bagasse [57], coconut burch waste [58], and papaya seed [59] have been investigated for the removal of pollutants from aqueous solutions.

Rice husk as obtained from a local rice mill grounded, sieved, washed and then dried at 80 _C was used by McKay et al. [60] for removal of two basic dyes: safranine and methylene blue and absorption capacity of 838 and 312 mg/g was found. Batzias and Sidiras [61] studied beech saw dust as low-cost absorbent for the removal of methylene blue and basic red 22 (1.4–14, 2.1–21 mg/L). In order to know the effect of chemical treatment and to improve its efficiency the authors also tested the potential of the absorbent by treating it with CaCl2 [61], using mild acid hydrolysis [62] and found it to increase the absorption capacity. Further studies to evaluate the effect of pH were also carried out by Batzias et al. [63]. Shi et al. [64] improved the absorption capacity of sunflower stalks by chemically grafting quaternary ammonium groups on them. The modified sunflower stalks exhibited increased absorption capacity for anionic dyes, due to the existence of quaternary ammonium ions on the surface of the residues. The maximum absorption capacities on modified sunflower stalks were found to be 191.0 and 216.0 mg/g for Congo red and direct blue, respectively, which were at least four times higher than that observed on unmodified sunflower stalks. Further, the same authors observed that absorption rates of two direct dyestuffs were much higher on the modified residues than on unmodified ones. A comparison of various low-cost absorbents derived from different agricultural wastes for the removal of diverse types of aquatic pollutants is summarized in Table 2.2.

Industrial Waste: Widespread industrial activities generate huge amount of solid waste materials as by-products. Industrial wastes such as sludge, fly ash, and red mud are classified as low-cost materials, locally available and can be used as absorbents for removal of
pollutant from aqueous solution [65]. Fly ash is a waste material originating in combustion processes. Although it may contain some hazardous substances, such as heavy metals, it has been showing good absorption qualities for phenolic compounds [66]. The maximum phenol absorption capacity has been found to be 27.9 mg/g for fly ash and 108.0 mg/g for granular activated carbon at initial phenol concentration of 100 mg/L. Wang et al. [67] used fly ash as absorbent for the removal of methylene blue from aqueous solution reporting an absorption

capacity of 4.47 mg/g. The effect 28 M. Grassi et al. of physical (heat) and chemical treatment was also studied on as-received fly ash. The heat treatment was reported to have adverse effect on the absorption capacity of fly ash but acid treatment (by nitric acid) resulted in an increase of absorption capacity of fly ash (7.99 mg/g). Bhatnagar and Jain [9] investigated steel and fertilizer industries wastes, as an absorbent for the absorption of cationic dyes. It was found that the absorbents prepared from blast furnace sludge, dust and slag have poor porosity and low surface area, resulting in very low efficiency for absorption of dyes. Smith et al. [76] reported that chemical activation using alkali metal hydroxide reagents, especially KOH, was found to be the most effective technique for producing high BET surface area sludge-based absorbents (in excess of 1,800 m2/g). Red mud is a waste material formed during the production of alumina [77]. Red mud has been explored as an alternate absorbent for arsenic. An alkaline aqueous medium (pH 9.5) favored As(III) removal, whereas the acidic pH range (1.1–3.2) was effective for As(V) removal [78, 79]. A comparison of various low-cost absorbents derived from different industrial wastes for the removal of diverse types of aquatic pollutants is summarized in Table 2.3. 2.4 Absorption as Green Technology The literature studies showed above highlighted that absorption process can be considered an efficient treatment for the removal of emerging compounds from water. It allows to reach good removal percentage and, furthermore, being a physical process, does not imply by-products formation, which could be more toxic than parent compounds. It is obvious that absorption process is encompassed in an integrated treatment system which involves many factors, such as available space for the construction of treatment facilities, waste disposal constraints, desired finished water quality, and capital and operating costs. All these factors imply the achievement of the optimal operating conditions for low-cost high efficiencies [10, 80]. The most used and studied absorbents are certainly activated carbons both for synthetic and real water (surface water and wastewater). In spite of large use of them, the overall idea is to reduce the use of activated carbon because of high costs. Therefore, scientific world is looking for low-cost absorbents for water pollution. In addition to cost problem, another important factor pushing toward low-cost absorbents is the use of agricultural and industrial waste products in order to extend the life of waste materials without introducing into the environment new materials as absorbents and to reduce costs for waste disposal therefore contributing to environmental protection. Anyway a suitable non-conventional low-cost absorbent should:

(1) be efficient to remove many and different contaminants,
(2) have high absorption capacity and rate of absorption, and
(3) have high selectivity for different concentrations.

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It is very difficult to understand which absorbent is better because they have different properties (porosity, surface area, and physical strength) as well as different absorption capacities related to experimental conditions [94]. Absorbent cost is an important parameter to compare different materials. In Fig. 2.4 costs of several low-cost and commercial absorbents are shown. They should be considered indicative because of absorbent costs depend on many factors such as its availability, its source (natural, industrial/agricultural/ domestic wastes or by-products or synthesized products), treatment conditions, and recycle and lifetime issues. Furthermore, the cost also depends on when absorbents are produced in (or for) developed, developing, or underdeveloped countries [95]. Finally, a right cost evaluation is related to the application scale and, although many studies about non-conventional low-cost absorbents are available in the literature, they are limited to laboratory scale. Thus, cost estimation is not strictly right and pilot-plant studies should also be conducted utilizing low-cost absorbents to check their feasibility on commercial scale.

Concluding Remarks: The economical and easily available absorbent would certainly make an absorption-based process a viable alternative for the treatment of wastewater containing

pollutants. Selection of an appropriate absorbent is one of the key issues to achieve the maximum removal of type of pollutant depending upon the absorbent and Fig. 2.4 Cost of several absorbents. The image contains the references to the respective absorbents in square brackets [6, 49, 50, 86–93] 32 M. Grassi et al.

absorbate characteristics. The effectiveness of the treatment depends not only on the properties of the absorbent and absorbate, but also on various environmental conditions and variables used for the absorption process, e.g. pH, ionic strength, temperature, existence of competing organic or inorganic compounds in solution, initial absorbate and absorbent concentration, contact time and speed of rotation, particle size of absorbent, etc.

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