



Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review



Sabino De Gisi^{a,*}, Giusy Lofrano^{a,b}, Mariangela Grassi^b, Michele Notarnicola^a

^a Department of Civil, Environmental, Land, Building Engineering and Chemistry (DICATECh), Technical University of Bari, Via E. Orabona n. 4, 70125 Bari (BA), Italy

^b Department of Chemistry and Biology, University of Salerno, via Giovanni Paolo II, 132 84084 Fisciano, (Salerno), Italy

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ABSTRACT

Low-cost by-products from agricultural, household and industrial sectors have been recognized as a sustainable solution for wastewater treatment. They allow achieving the removal of pollutants from wastewater and at same time to contribute to the waste minimization, recovery and reuse. Despite numerous reviews have been published in the last few years, a direct comparison of data obtained using different sorbents is difficult nowadays because of inconsistencies in the data presentation. In this context, the aim of the study was to revise the current literature concerning the application of low-cost adsorbents for wastewater treatment highlighting, systematically, both adsorbents characteristics and adsorption capacities. For this scope, low-cost sorbents have been divided into the following five groups: (i) Agricultural and household wastes, (ii) industrial by-products, (iii) sludge, (iv) sea materials, (v) soil and ore materials and (vi) novel low-cost adsorbents. The affinity of sorbents in removing various pollutants, their applications on real wastewater, costs and considerations on their reuse after adsorption processes, has been discussed. Finally, in order to better highlights the affinity of sorbents for more pollutants (dyes, heavy metals, biorecalcitrant compounds, nitrogen and phosphate compounds), simple methodological tools such as “adsorbents-pollutants” matrices have been proposed and applied. In this manner, the adsorbent candidates for replacing commercial activated carbons have been identified.

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Contents

1. Introduction and scope	10
2. Adsorption process	12
2.1. Mechanisms and definitions	12
2.2. Characteristics of activated carbons	12
3. Low costs adsorbents	12
3.1. Agricultural and household waste	12
3.2. Industrial waste	20
3.3. Sludge	25
3.4. Sea materials	26
3.5. Soil and ore materials	28
3.6. Novel low costs adsorbents	30
4. Outlooks and discussion	30
5. Concluding notes	37
Acknowledgment	37
Appendix A. Supplementary data	37
References	37

1. Introduction and scope

Over the years, the quality of water is deteriorating mainly due to the anthropogenic activities, population growth, unplanned urbanization, rapid industrialization and unskilled utilization of natural water

* Corresponding author.

E-mail address: sabino.degisi@poliba.it (S. De Gisi).

resources. Furthermore, the increased awareness of the importance of providing impacts due to the current environmental strategies has pushed the research community towards the development of robust, economically feasible and environmentally friendly processes capable of removing pollutants from water and at same time to safeguard the health of affected populations [1].

A variety of treatment technologies are available with different degree of success to control and minimize water pollution [2]. However, the shortcomings of most of these methods are high operational and maintenance costs, generation of toxic sludge and complicated procedure involved in the treatment [3]. Comparatively, adsorption process is considered a better alternative in water and wastewater treatment because of convenience, ease of operation and simplicity of design [3,4,5]. In wastewater treatment plants (WWTPs), adsorption processes are applied for the removal of dissolved pollutants that remain from the subsequent biological phases or after chemical oxidation treatments. Today, the most commonly adopted adsorbent is the activated carbon. It is commonly used for the removal of various pollutants from water such as

dyes and heavy metals [1; 2]. However, its widespread use in wastewater treatment is sometimes restricted due to its higher cost [4] besides other issues such as the adsorbent regeneration capacity or the disposal of the end-of-life sorbent following different strategies than disposal [6].

A large variety of low-cost adsorbents have been examined for their ability to remove various types of pollutants from water and wastewater. Generally, the goal is to replace activated carbons – representing the state-of-the-art – by means of a by-products coming from various activities such as agriculture and industry. These by-products currently pose a variety of disposal problems due to their bulk volume, toxicity or physical nature (i.e., petroleum wastes, scrap tyres, rice hulls). If these wastes could be used as low-cost adsorbents, it will provide a two-fold advantage to environmental pollution. Firstly, the volume of by-products (or wastes) could be partly reduced and secondly the low-cost adsorbent, if developed, can reduce the pollution of wastewaters at reasonable cost [1].

Over the last few decades, several literature reviews concerning the use of low-cost adsorbents for wastewater treatment have been published as shown in Table 1.

Table 1

Review articles concerning low-cost adsorbents in the field of separation science published in the years 2009–2016.

N.	References	Goal	Type of adsorbent ^(a)	Pollutants being investigated
1	Ungureanu et al. [7]	The review presented a state of the art of adsorption techniques for arsenic and antimony removals from water and wastewater.	Agricultural and household wastes; Industrial wastes; Sea materials; soil and ore materials; metal oxides and hydroxides	Arsenic and antimony
2	Çifçi and Meriç [8]	The study aimed to review the scientific literature of pumice stone with the particular focus on its use for the treatment of water and wastewater.	Soil and ore materials	Various pollutants
3	Bhatnagar et al. [3]	The review compiles the work conducted by various researchers over the last few decades on the use of various agricultural waste peels as adsorbents for the water and wastewater treatment. In this review, adsorption capacities for organic and inorganic pollutants by different peel-based adsorbents are summarized.	Agricultural and household waste	Dyes; heavy metals
4	Gautam et al. [4]	The review provided a comprehensive appraisal of the equilibrium modeling of a number of biosorption processes as well as the structural, chemical and morphological modifications and activation of biosorbents.	Agricultural and household wastes; sea materials	Heavy metals
5	Abdolali et al. [9]	The review deals with utilization of typical low cost wastes and by products produced in different food agricultural and agro-industries as biosorbent and reviews the current state of studies on a wide variety of cheap biosorbents in natural and modified forms.	Agricultural and household	Heavy metals
6	Yagub et al. [10]	The review article provides extensive literature information about dyes, its classification and toxicity, various treatment methods, and dye adsorption characteristics by various adsorbents.	Agricultural and household wastes; industrial wastes; soil and ore materials	Dyes
7	Anastopoulos and Kyzas [11]	The review summarizes the recently published literature (after 2010) regarding the use of agricultural peels for dye adsorption.	Agricultural and household	Dyes
8	Rangabhashiyam et al. [12]	The review article focuses on the various sources of the agricultural waste products and its adsorption capacity of the different dyes.	Agricultural and household	Dyes
9	Nguyen et al. [13]	The review discusses the potential use of agricultural waste based biosorbents (AWBs) for sequestering heavy metals in terms of their adsorption capacities, binding mechanisms, operating factors and pretreatment methods.	Agricultural and household	Heavy metals
10	Bilal et al. [14]	The review is dedicated to presenting state of the art knowledge on various bioadsorbents and physico-chemical conditions used to remediate Cu ²⁺ from waste streams.	Agricultural and household	Copper
11	Ali et al. [5]	The review described the conversion of waste products into effective adsorbents and their application for water treatment	Agricultural and household wastes; industrial waste; sea materials; soil and ore materials; metal oxides and hydroxides	Organic pollutants
12	Bhatnagar and Sillanpää [15]	In this review, an extensive list of low-cost adsorbents (prepared by utilizing different types of waste materials) from vast literature has been compiled and their adsorption capacities for various aquatic pollutants as available in the literature are presented.	Activated carbon; agricultural and household wastes; Industrial wastes; Sludge;	Various pollutants (Dyes; heavy metals; PAHS)
13	Foo and Hameed [16]	The paper presented a state of the art review of the rice milling industry, its background studies, fundamental properties and industrial applications. Moreover, the key advance on the preparation of novel adsorbents, its major challenges together with the future expectation has been highlighted and discussed.	Agricultural and household waste; industrial waste (agro food industry).	Various pollutants
14	Gupta and Suhas [17]	This review highlights and provides an overview of these low cost adsorbents (LCAs) comprising natural, industrial as well as synthetic materials/wastes and their application for dyes removal.	Activated carbon; agricultural and household wastes; sludge; sea materials; soil and ore materials.	Dyes

Bhatnagar et al. [3] investigated the use of various agricultural waste peels as adsorbents for the removal of organic (dyes) and inorganic (heavy metals) pollutants from wastewater. Gautam et al. [4] focused on the removal of heavy metals from wastewater by means of agriculture and household wastes, highlighting, moreover, equilibrium modeling of a number of biosorption processes as well as the structural, chemical and morphological modifications and activation of biosorbents. Yagub et al. [10] studied dyes, their classification and toxicity, various treatment methods and dye adsorption characteristics by various adsorbents such as agricultural, industrial and soil and ore. Instead, Bhatnagar and Sillanpää [15] investigated the use of low-cost sorbents coming from different activities (mainly industrial) for the removal of further pollutants such as polycyclic aromatic hydrocarbons.

Despite numerous reviews, Gautam et al. [4] highlights how, to date, a direct comparison of data obtained using different sorbents is difficult because of inconsistencies in the data presentation. Thus, taking into account this situation, the aim of the study was to revise the current literature concerning the application of low-cost adsorbents for wastewater treatment highlighting, systematically, both adsorbents characteristics and adsorption capacities.

For this scope, low-cost sorbents have been divided into the following groups according to Ali et al. [5]: (i) Agricultural and household by-products, (ii) industrial by-products, (iii) sludge, (iv) sea materials, (v) soil and ore materials and (vi) novel low-cost adsorbents. To the best of our knowledge, no study that deepening in a systematic manner the cluster of by-products in terms of adsorbent characteristics and adsorption capacities, has been published.

Even further, the affinity of sorbents in removing various pollutants, the applications of such low-cost sorbents on real wastewater, the cost of sorbents as well as considerations on the reuse of sorbents after adsorption processes, have been discussed. In order to better highlight the affinity of sorbents for more pollutants, simple methodological tools such as “adsorbents-pollutants” matrices have been proposed and applied.

The article is structured in such a way that information on adsorption processes and commonly used activated carbons in terms of sorbent characteristics (state-of-the-art) are reported in Section 2. Instead, the five groups of low-cost adsorbents as well as their adsorption capacities in terms of characteristics and pollutants removal from wastewater are described in the Section 3. Finally, Sections 4 and 5 consist in the discussion and conclusion sections, respectively.

2. Adsorption process

2.1. Mechanisms and definitions

Adsorption 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 *adsorbate* and the adsorbing material is termed the *adsorbent*. The properties of adsorbates and adsorbents are quite specific and depend upon their constituents. 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 adsorbed substance. On the other hand, if the attraction forces between adsorbed molecules and the solid surface are due to chemical bonding, the adsorption process is called *chemisorption*. Contrary to physisorption, chemisorption 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 adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, this process is exothermic [18].

In a solid–liquid system adsorption 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 adsorbed on the solid phase. The amount of adsorbate that can be taken up by an adsorbent as a function of both temperature and concentration of adsorbate, and the process, at constant temperature, can be described by an adsorption isotherm according to the general Eq. (1):

$$q_t = (C_0 - C_t) \cdot V/m \quad (1)$$

where q_t (mg/g) is the amount of adsorbate per mass unit of adsorbent at time t , C_0 and C_t (mg/l) is the initial and at time t concentration of adsorbate, respectively, V is the volume of the solution (l), and m is the mass of adsorbent (g) [18]. Several adsorption isotherms are reported in literature [19] although not detailed in this article.

2.2. Characteristics of activated carbons

As stated in Section 1, activated carbon is one of the most effective media for removing a wide range of contaminants from industrial and municipal waste waters, landfill leachate and contaminated groundwater. As the world's most powerful adsorbent, it can cope with a wide range of contaminants. Different contaminants may be present in the same discharge and carbon may be used to treat the total flow, or it may be better utilized to remove specific contaminants as part of a multistage approach.

The activated carbon is produced from various raw materials and, therefore, it presents different properties [20]. Apart from the raw material, the specific properties of the coal also depend on the particular activation process employed, which may be conducted by physical processes, by contact with a high temperature steam flow (800–1000 °C) or, by chemical with use of acids. The bulk density may be used in order to identify several activated carbon classes. The macroporous carbon has a bulk density >1 cm³/g (pore space volume for gram of carbon). The mesoporous carbon has a bulk density in the range 0.85–1.0 cm³/g. Instead, the microporous carbon presents a value <0.85 cm³/g. Generally, macroporous or mesoporous carbons are used for the removal of large molecules while, microporous, are more suitable for the removal of small molecules [2,20]. The content of ash, another characteristics parameter, depends on the raw material used. Generally, its value increases with the number of regeneration cycles, with a percentage increase of 0.5–1.0% for each cycle. This involves a consequent limitation of the number of possible regenerations. For activated carbons, the content of ash is <15%. The Iodine number is an index of the ability of the sorbent to adsorb small molecules, expressed in mg of iodine adsorbed per gram of carbon. For activated carbons, the Iodine number varies in the range 500–1200 mg/g. Finally, another important parameter is the specific surface area expressed in m²/g. Generally, adsorption capacities increase with the growth of this parameter. In the case of activated carbons, the specific surface area varies in the range 500–1500 m²/g [20].

3. Low costs adsorbents

3.1. Agricultural and household waste

The agricultural solid wastes from cheap and readily available resources such as agave bagasse [21,22,23], almond shell [24], apricot shell [24], barley straw [25], cashew nut shell [26], citric acid [25,27], corn cob [21], cotton and gingelly seed shell [28], depectinated pomelo peel [29], Egyptian mandarin peel [30], fruit juice residue [31], garden grass [32], garlic peel [33], grapefruit peel [34], hazelnut shell [35], lentil shell [36], mango peel waste [37], Mosambi (*Citrus limetta*) peel [38], muskmelon peel [39], pine sawdust [40], pongam seed shell [41], groundnut shell [42], olive stone [43], plum kernel [21], pomegranate peel [44], pomelo peel [29], potato peel [45], rice shell [36], rice straw [46], sugarcane bagasse [47,48], walnut shell [35], banana peel [49],

cane pith [51], coir pith [52], yellow passion fruit [53], orange peel [27, 49,54,55–57], rice husk [31,58,59,60–63], sawdust carbon [58], soy meal hull [64], sunflower stalk [65], white ash [66], white rice husk ash [60], wood derived biochar [63], biomass *Euphorbia rigida* [67], pinewood [68], mixture almond shells [69], cassava peels [70], ash gourd peel [71], Cucumis sativa peel [72], lentil husk [73], neem bark [74], pomegranate peel [75], sunflower hull [76], wheat stem [77], carbon cloth [78], sky fruit husk [79] and coconut shells [80] have been investigated for the removal of numerous dyes from aqueous solutions. The basic components of the agricultural waste materials include hemicelluloses, lignin, lipids, proteins, simple sugars, water, hydrocarbons and starch, containing a variety of functional groups with a potential sorption capacity for various pollutants [3,15]. Agricultural waste products are used in the natural and modified form. In the natural form, the product is washed, ground and sieved until reaches the desired particle size and subsequently used in adsorption tests. While, in the modified form, the product is pre-treated by means of well known modification techniques [15]. The goal of these pre-treatments is to enhance and reinforce the functional group potential and, consequently, increase the number of active sites. Agricultural waste products have been extensively studied in relation to the adsorption process.

Below, the most significant experiences are described, starting from agriculture and household waste sorbents for the removal of dyes from single compound aqueous solution.

Aygun et al. [24] investigated the use of almond shell, hazelnut shell, walnut shell and apricot stone as raw materials for granular activated carbon (GAC) production. GACs were evaluated for their physical (attrition, bulk density), chemical (elemental composition, % weight loss), surface (surface area, surface chemistry) and adsorption properties (iodine number, phenol and methylene blue adsorption). Results showed that their suitability for GAC production is not determined by material specific (elemental composition) but type-specific features. Furthermore, pyrolysis temperature and activation time with $ZnCl_2$ had influence on the methylene blue adsorption capacities of especially for the activated carbons produced from hazelnut and walnut shells. They obtained the following order of suitability of raw materials for GACs production: hazelnut shell > walnut shell ~ apricot stone > almond shell. Juang et al. [21] studied the adsorption of two commercial dyes (Acid blue 25 and Basic red 22) from water on activated carbons at 30 °C. The carbons were prepared from bagasses and were activated by steam with different extents of burn-off by varying the temperature in the range of 750–840 °C. The resulting carbons were ground in a mill followed by washing and drying. Results showed that the pore diameters for the present bagasse-based carbons were mostly <2 nm (micropore), but had a peak of near 4 nm (mesopore). In addition, the volume fraction of meso-/macropores increased from 22.3 to 31.1% with increasing the extent of burn-off from 80.6 to 91.3 wt%. The iodine number of the carbons, as well as the adsorption capacities for the two investigated dyes, increased with increasing the extent of burn-off. Thinakaran et al. [28] studied the removal of Acid Red 114 (AR 114) from aqueous solutions using activated carbons prepared from gingelly (sesame) (Sp), cotton (Cp) and pongam (Pp) seed shells. The raw materials were repeatedly washed with distilled water to remove dirt, dust and other surface impurities. The washed seed shells were dried in the sun for 48 h, cut into small pieces, soaked in 18 N sulphuric acid (1:2, w/v), and heated separately for 24 h at 80 °C in a Muffle furnace. After treatment, all the treated samples were cooled to room temperature and washed with distilled water until the filtrates attained neutral pH. The resulting activated carbon materials (ACSS) were dried in a hot air oven at 105 °C, powdered and sieved through a 0.25 mm sieve. Results showed that optimum conditions for AR 114 removal were found to be pH 3, adsorbent dosage of 3 g/l and equilibrium time of 4 h. Higher removal percentages were observed at lower concentrations of AR 114. Furthermore, the adsorption capacity of the studied adsorbents was in the order Sp > Cp > Pp.

The adsorption of malachite green (MG) from aqueous solution by two different adsorbents (CZn5, PETNa8) were studied by Akmil-Başar et al. [40]. Adsorbents were prepared from pine sawdust and polyethyleneterephthalate (PET) by chemical activation with $ZnCl_2$ and NaOH, respectively. The adsorption was carried out in a batch system as a function of dye concentration, pH and contact time. Both adsorbents were found to be very effective in removing the dye at high concentration with adsorption percentage in the order of CZn5 > PETNa8. The pH of dye solution in the range of 6–10, was found favorable for the removal of malachite green by using the two adsorbents at high concentrations. Equilibrium times were 120 and 90 min for CZN5 and PETNa8, respectively. Malik et al. [42] investigated groundnut shell for the preparation of an adsorbent by chemical activation using $ZnCl_2$ under optimized conditions. Characteristics of the novel activated carbon were compared with commercially available powdered activated carbon (CPAC). The groundnut shell-based powdered activated carbon (GSPAC) has a higher surface area (1114 m²/g), iodine and methylene blue number compared to CPAC. Both of the carbons were used for the removal of malachite green dye from aqueous solution and the effect of various operating variables such as adsorbent dose (0.1–1 g/l), contact time (5–120 min) and adsorbate concentrations (100–200 mg/l) on the removal of dye, was studied. The experimental results indicate that at a dose of 0.5 g/l and initial concentration of 100 mg/l, GSPAC showed 94.5% removal of the dye in 30 min equilibrium time, while CPAC removed 96% of the dye in 15 min.

Physical properties of activated carbons prepared from pinewood at different activation times (0.5, 1.5, 2.7, and 4.0 h) in steam at 900 °C were studied by Tseng et al. [68]. The adsorption equilibrium and kinetics of three dyes (Acid blue 264, Basic blue 69, Methylene blue) from aqueous solutions on such carbons were then examined at 30 °C. After activation, the pinewood-products were ground in a mill followed by washing with water and drying. Subsequently, they were sieved in the size range 0.12–0.20 mm. The maximum adsorption capacities were 1176, 1119 and 556 mg/g for Acid blue 264, Basic blue 69 and Methylene blue, respectively. Annadurai et al. [49] prepared banana and orange peels as adsorbents for the adsorption of dyes. The peels were dried, crushed, and washed thoroughly with deionized water to remove the adhering dirt. They were air dried in an oven at 100–120 °C for 24 h. After drying, the adsorbent was sieved through a 5 mm mesh size. The densities of banana and orange peels were 1.72 and 1.47 g/ml, respectively while, the specific surface areas of both peels were in the range 20.6–23.5 m²/g. Results showed that the adsorption capacities for both peels decreased in the order methyl orange (MO) > methylene blue (MB) > Rhodamine B (RB) > Congo red (CR) > methyl violet (MV) > amido black 10B (AB).

The yellow passion fruit (*Passiflora edulis Sims. f. flavicarpa Degener*) (YFPWF), a powdered solid waste, was tested as biosorbent for the removal of Methylene blue (MB). The waste peel was extensively washed with water and dried under sunlight for 48 h. Afterwards, the yellow passion peel was crushed in a knife-mill. The resulting material was sieved, and the portion with particle diameter lower than 250 µm, was subsequently washed with doubly distilled water for 10 min, and then dried in an oven at 60 °C for 24 h. Powdered material was preserved in the desiccator and used in the adsorption studies. Adsorption of MB onto this natural adsorbent was studied by batch adsorption at 25 °C. Results showed that in alkaline pH region the adsorption of MB was favorable and the contact time required to obtain the maximum adsorption was 48 h. The maximum amount of MB adsorbed on YFPWF biosorbent was 44.67 mg/g [53]. Activated carbons, prepared from mahogany sawdust and rice husk was utilized as the adsorbents for the removal of Acid Yellow 36. Results showed that a pH value of 3 is favorable for the adsorption of acid dye. The adsorption capacities of sawdust carbon and rice husk carbon were found to be 183.8 mg and 86.9 mg per g of the adsorbent, respectively [58]. The application of soy meal hull (SMH) for the removal of direct and acid dyes from aqueous solutions was investigated by Arami et al. [64]. Four textile dyes, Direct red 80 (DR80), Direct red 81 (DR81), Acid blue 92 (AB92)

and Acid red 14 (AR14) were used as model compounds. Results showed that the pH value of 2 is favorable for the adsorption of all four dyes. The adsorption capacities of SMH for DR80, DR81, AB92 and AR14 were, 178.57, 120.48, 114.94 and 109.89 mg/g of adsorbent, respectively. Based on the obtained data, authors concluded that SMH is a natural, eco-friendly and low-cost adsorbent with relatively large adsorption capacity suitable for the removal of dyes from colored aqueous solutions. Ezechi et al. [81] studied the adsorption capacity of a neglected adsorbent named *Ageratum conyzoides leaf powder*. Collected in a rural area of Malaysia, the leaves were severally washed with distilled water to remove surface particles and impurities, before to be dried under sunlight for 48 h and placed in the oven at 60 °C for 24 h. The dried leaves were grounded with a domestic mixing grinder and sieved to particle size of 75–100 µm. The leaf powder was washed severally with distilled water (15 times) to remove chlorophyll pigments and redried in the oven at 60 °C for 24 h. Finally, the dried *Ageratum conyzoides leaf powder* was stored in a container for use. The obtained results showed how the optimal conditions were pH 4, adsorbent concentration 0.06 g and 20 min contact time which yielded methylene blue removal of 91% at initial methylene blue concentration of 20 mg/l.

Gürses et al. [82] studied the capacity of untreated lignite (Aşkale lignite) for the removal of methylene blue highlighting how the adsorption capacity increased with the increasing temperature, initial dye concentration, pH and ionic strength, although it was not affected by the stirring speed. They showed how, with reference to a contact time of 20 min, adsorbent amount of 0.15 g, temperature of 20 °C, agitation rate of 150 min⁻¹, pH natural, the adsorption capacity related to an initial adsorbate concentration of 10, 20, 40, 60, 80 and 100 (values in mg/l) was about 7 mg/g, 13 mg/g, 22.5 mg/g, 26 mg/g, 29 mg/g and 32 mg/g, respectively.

Shi et al. [83] improved the adsorption capacity of sunflower stalks by chemically grafting quaternary ammonium groups on them. The modified sunflower stalks exhibited increased adsorption capacity for anionic dyes, due to the existence of quaternary ammonium ions on the surface of the residues. The maximum adsorption capacities on modified sunflower stalks were found to be 191 and 216 mg/g for Congo red and direct blues, respectively, which were at least four times higher than that observed on unmodified sunflower stalks. Further, the same authors observed that adsorption rates of two direct dyestuffs were much higher on the modified residues than on unmodified ones. Tavlieva et al. [60] studied the adsorption kinetics of brilliant green onto white rice husk in aqueous solutions. They showed that the maximum adsorption capacity at 47 °C was 85.56 mg/g. Further, considering a contact time of 60 min and an adsorbent dosage of 5 g/l, the adsorption capacity related to an initial adsorbate concentration of 3, 6, 8, 20, 40 and 100 mg/l was about 0.8 mg/g, 0.9 mg/g, 1.0 mg/g, 3.0 mg/g, 7.0 mg/g and 18 mg/g, respectively. Moreover, Tavlieva et al. [60] highlighted how the temperature increase favored the removal, and the brilliant green adsorption was a fast process at 47 °C, as it reached equilibrium within 90 min.

The adsorption of Rhodamine-B (RhB) onto treated rice husk-based activated carbon was investigated by Ding et al. [59]. The rice husk was mixed with phosphoric acid (50 wt%) in a mass ratio (rice husk to phosphoric acid) of 1:4, then the mixture was heated to 500 °C and maintained 1 h and the obtained product was treated in different modes. In the first mode, with the production of an adsorbent named P-AC, rice husk was washed with distilled water until neutral pH. In the second mode, the rice husk was washed with hot distilled water (95 °C) until neutral pH and the resulting solid product was named as P95-AC. Finally, in the third mode, the solid product was washed with distilled water until neutral pH and mixed with 3 wt% potassium hydroxide solution. Then, the mixture was heated to boiling under reflux condition, and maintained 1 h. The solid product was separated from liquid product by filtration and labelled PK-AC. Another activated carbon was produced by KOH activation, where the mass ratios of rice husk to KOH was 1:4. The reaction was conducted at 400 °C for 0.5 h,

and then 800 °C for 1 h and the corresponding activated carbon was named K-AC. The adsorption capacities as well as some characteristics of the investigated adsorbents are shown in Table 2. Results demonstrated that PK-AC was an effective adsorbent for removal of RhB from aqueous solution. Initial RhB concentration and temperature played important roles in this adsorption process, and pH had a little effect on RhB adsorption.

Furthermore, Table 2 synthesizes the main characteristics of sorbents as well as their adsorption capacities with reference to agriculture and household waste applied for the removal of dyes. Generally, for each adsorption test, the specific surface area and the particle size range, was reported. Instead, information related to the production of sorbents, can be derived directly from the linked references.

Table 2 shows how specific surface area is for 6.1%, 20.4%, 16.3%, 32.7% and 24.5% in the range of 0–10, 11–100, 101–500, 501–1000 and >1000 m²/g, respectively. The maximum surface corresponds to the case of treated rice husk-based activated carbon (named K-AC) with a value of 2516 m²/g. This highlights how adsorption capacity generally increases with the use of adequate pre-treatments. Adsorbent dose is in the range of 0.01–10 g/l with a typical value of 1 g/l, corresponding to the 41.5% of the investigated cases. Higher values are in the case of high initial pollutants concentrations. Temperature varies in the range of 19.8–46.8 °C. On 38 available data, only two cases refer to hot processes based on temperature around 40 °C. However, as shown in Table 2, the available information is not always complete in line with Gautan et al. [4] with reference to the quality of data for the goal of an adsorbents comparative assessment.

The most significant experiences related to the use of agriculture and household waste sorbents for the removal of heavy metals from single compound aqueous solution are herein described. Lignocellulosic materials have a very complex configuration that contains a variety of active sites capable, in some cases, of adsorbing contaminants from water. Agave bagasse is a sub-product from the alcohol industry that has been very little studied, but that could have the potential to remove a variety of contaminants from aqueous solutions. Raw and modified *Agave salmiana bagasse* was tested to remove metal cations by Velazquez-Jimenez et al. [23]. HCl, HNO₃, NaOH, tartaric, citric and oxalic acids were used to modify bagasse to determine if its concentration of active groups could be improved. These materials were tested for the removal of Cd(II), Pb(II) and Zn(II) ions from water at pH 5, and desorption studies were performed at pH 2 and 4 at 25 °C. The characterization techniques mainly identified carboxyl, hydroxyl, sulfur and nitrogen containing groups in bagasse. Authors showed that mainly the carboxylic groups were responsible for metal uptake. Raw bagasse has an adsorption capacity of about 8, 14 and 36 mg/g for zinc, cadmium and lead, respectively, and this was improved about 27–62% upon modification with HNO₃ and NaOH. Treatments with citric, oxalic and tartaric acid did not have a significant effect in adsorption capacities. Furthermore, raw agave bagasse has a very acceptable adsorption capacity of metal cations and it can approximately be regenerated in a 45%, since the biosorption mechanism involves ion exchange and complexation. Ash gourd (*Benincasa hispida*) is a commonly consumed vegetable in the Asian subcontinent, known to possess a good medicinal value. Sreenivas et al. [71] investigated the utilization of ash gourd (defatted) peel in biosorption of chromium (Cr), also considering column operations. Peel powder was studied for particle size (446 µm), specific surface area (0.4854 m²/g) and other characteristics. In equilibrium studies at pH 1, >91% Cr (VI) gets adsorbed on ash gourd peel powder at an adsorbent dosage of 6 g/l for 125 mg/l solution. The sorption capacity of peel for Cr (VI) in batch studies was 18.7 mg/g. Feng et al. [54] chemically modified orange peel by means of hydrolysis of the grafted copolymer, which was synthesized by interaction of methyl acrylate with cross-linking orange peel. The adsorbent preparation procedure consists of several steps well described in Feng et al. [54]. The modified biomass was found to present high adsorption capacity and fast adsorption rate for Cu(II). The adsorption capacity was

Table 2

Main characteristics and uptake capacities of various agricultural and household waste sorbents for dyes removal.

N.	Adsorbent		Adsorption test						References	
	Type	Characteristics	Pollutants to be removed	Adsorbent dose	Initial pollutant concentration range	Contact time	Temperature	pH		Amount adsorbed (q _e)
1	AC-almond shell (ACA)	Specific surface area = 783.0 m ² /g	Basic blue 9 (Methylene blue)	-	-	24 h	-	-	1.33 mg/g	[24]
2	AC-Apricot shell (ACAS)	Specific surface area = 783.0 m ² /g	Basic blue 9	-	-	24 h	-	-	4.11 mg/g	[24]
3	AC-Bagasse	Specific surface area = 607 m ² /g	Acid blue 25 (C.I. N. 62,055)	1 g/l	-	-	30 °C	6.1	674 g/kg	[21]
4	AC-Bagasse	Specific surface area = 1433 m ² /g	Acid blue 80	0.01 g/l	20–1050 mg/dm ³	21 days	-	7.4	391 mg/g	[22]
5	AC-Bagasse	Specific surface area = 607 m ² /g	Basic red 22 (C.I. 11,055)	1 g/l	-	-	30 °C	4.1	942 mg/g	[21]
6	AC-Corn cob	Specific surface area = 943 m ² /g	Acid blue 25 (C.I. N. 62,055)	1 g/l	-	-	30 °C	6.1	1060 mg/g	[21]
7	AC from biomass <i>Euphorbia rigida</i>	Specific surface area = 741 m ² /g	Disperse orange 25	2 g/l	-	-	20 °C	7.0	118.93 mg/g	[67]
8	AC from cotton seed shell	Specific surface area = 124.35 m ² /g	Acid red 114	1 g/l	100 mg/l	240 min	-	3.0	153.85 mg/g	[28]
9	AC from gingelly seed shell	Specific surface area = 229.65 m ² /g	Acid red 114	1 g/l	100 mg/l	240 min	-	3.0	102.04 mg/g	[28]
10	AC from pine sawdust (CZn5)	Specific surface area = 1390 m ² /g	Basic green 4 (Malachite green)	5 g/l	50–2000 mg/l	120 min	26 °C	6–10	370.37 mg/g	[40]
11	AC from pine sawdust (PETNa8)	Specific surface area = 410 m ² /g	Basic green 4	5 g/l	50–2000 mg/l	90 min	26 °C	6–10	-	[40]
12	AC from pongam seed shell	Specific surface area = 324.79 m ² /g	Acid red 114	1 g/l	100 mg/l	240 min	-	3.0	204.08 mg/g	[41]
13	AC-groundnut shell	Specific surface area = 1114 m ² /g	Basic green 4	0.5 g/l	100 mg/l	30 min	-	-	222.2 mg/g	[42]
14	AC-Hazelnut shell (ACH)	Specific surface area = 793.0 m ² /g	Basic blue 9	-	-	24 h	-	-	8.82 mg/g	[35]
15	AC-Plum kernel	Specific surface area = 1162 m ² /g	Acid blue 25 (C.I. N. 62,055)	1 g/l	-	-	30 °C	6.1	904 mg/g	[21]
16	AC-Plum kernel	Specific surface area = 1162 m ² /g	Basic red 22	1 g/l	-	-	30 °C	4.1	710 mg/g	[21]
17	AC-Pinewood	Specific surface area = 902 m ² /g	Acid blue 264 (AB264)	0.4 g/l	10–300 mg/l	5 days	30 °C	6.5	1176 mg/g	[68]
18	AC-Pinewood	Specific surface area = 902.0 m ² /g	Basic blue 69 (BB69)	0.4 g/l	10–300 mg/l	5 days	30 °C	5.4	1119 mg/g	[68]
19	AC-Pinewood	Specific surface area = 902.0 m ² /g	Basic blue 9	0.4 g/l	10–300 mg/l	5 days	30 °C	6.6	556 mg/g	[68]
20	AC-Sugarcane bagasse (CB100)	Specific surface area = 790 m ² /g	Acid orange 10 (C.I. 16,230)	0.2 g/l	14 mg/l	20 h	40 °C	-	5.78 mg/g	[47]
21	AC-Walnut shell (ACW)	Specific surface area = 774.0 m ² /g	Basic blue 9	-	-	24 h	-	-	3.53 mg/g	[35]
22	Banana peel	Specific surface area = 20.6–23.5 m ² /g	Direct red 28 (Congo red)	1 g/l	10–120 mg/l	24 h	30 °C	7.9	18.2 mg/g	[49]
23	Banana peel	Specific surface area = 20.6–23.5 m ² /g	Acid orange 52 (methyl orange)	1 g/l	10–120 mg/l	24 h	30 °C	5.7	21 mg/g	[49]
24	Banana peel	Specific surface area = 20.6–23.5 m ² /g	Basic blue 9	1 g/l	10–120 mg/l	24 h	30 °C	7.2	20.8 mg/g	[49]
25	Banana peel	Specific surface area = 20.6–23.5 m ² /g	Basic violet 10	1 g/l	10–120 mg/l	24 h	30 °C	5.8	20.6 mg/g	[49]
26	Cane (bagasse) pith	Specific surface area = 606.8 m ² /g	Acid blue 25 (C.I. N. 62,055)	-	-	5 days	-	6.9	673.6 mg/g	[51]
27	Cane pith	Specific surface area = 606.8 m ² /g	Basic red 22 (C.I. 11,055)	-	-	5 days	-	4.1	941.7 mg/g	[51]
28	Coir pith carbonized	Specific surface area = 259 m ² /g	Acid violet (C.I. 42,650)	8 g/l	10–40 mg/l	40 min	32 °C	1.5–10.4	8.06 mg/g	[52]
29	Coir pith carbonized	Specific surface area = 259 m ² /g	Rhodamine-B	7 g/l	10–40 mg/l	120 min	32 °C	2.1–11.1	2.56 mg/g	[52]
30	Yellow passion fruit	Specific surface area = 30 m ² /g	Basic blue 9	10 g/l	-	0.08–48 h	25 °C	8.0	44.67 mg/g	[53]
31	Mixture almond shells	Specific surface area = 10.5 m ² /g	Direct red 80	0.05–0.8 g/250 ml	50–150 mg/l	300 min	20 °C	6.0	22.422 mg/g	[69]
32	Orange peel	Specific surface area = 20.6–23.5 m ² /g	Acid orange 52	1 g/l	10–120 mg/l	24 h	30 °C	5.7	20.5 mg/g	[49]
33	Orange peel	Specific surface area = 20.6–23.5 m ² /g	Basic blue 9	1 g/l	10–120 mg/l	24 h	30 °C	7.2	18.6 mg/g	[49]
34	Orange peel	Specific surface area = 20.6–23.5 m ² /g	Basic violet 10	1 g/l	10–120 mg/l	24 h	30 °C	5.8	14.3 mg/g	[49]
35	Orange peel	Specific surface area = 20.6–23.5 m ² /g	Direct red 28	1 g/l	10–120 mg/l	24 h	30 °C	7.9	14.0 mg/g	[49]
36	Rice husk carbon (RHC)	Specific surface area = 272.5 m ² /g	Acid yellow 36 (C.I. 13,065)	-	-	180 min	30 °C	3.0	86.9 mg/g	[58]
37	Sawdust carbon (SDC)	Specific surface area = 516.3 m ² /g	Acid yellow 36 (C.I. 13,065)	-	-	60 min	30 °C	3.0	183.8 mg/g	[58]
38	Soy meal hull	Specific surface area = 0.7623 m ² /g	Acid blue 92	0.6 g/l	50–150 mg/l	1 days	20 °C	2.0	114.94 mg/g	[64]
39	Soy meal hull	Specific surface area = 0.7623 m ² /g	Acid red 14	0.7 g/l	50–150 mg/l	1 days	20 °C	2.0	109.89 mg/g	[64]
40	Soy meal hull	Specific surface area = 0.7623 m ² /g	Direct red 80	0.3 g/l	50–150 mg/l	1 days	20 °C	2.0	178.57 mg/g	[64]
41	Sunflower stalk	Specific surface area = 1.2054 m ² /g	Direct red 28	1.6 g/l	50–1000 mg/l	5 days	21 °C	-	37.8 mg/g	[65]
42	Sunflower stalk	Specific surface area = 1.2054 m ² /g	Direct blue 71	1.6 g/l	50–1000 mg/l	5 days	21 °C	-	26.8 mg/g	[65]
43	Sunflower stalk	Specific surface area = 1.2054 m ² /g	Basic blue 9	1.6 g/l	100–2000 mg/l	5 days	21 °C	-	205 mg/g	[65]
44	Sunflower stalk	Specific surface area = 1.2054 m ² /g	Basic Red 9	1.6 g/l	100–2000 mg/l	5 days	21 °C	-	317 mg/g	[65]
45	Treated rice husk-based activated carbon (named P-AC)	Specific surface area = 892 m ² /g	Rhodamine-B	10 g/l	300 mg/l	360 min	19.8 °C	1.3–10.2	170 mg/g	[59]
46	Treated rice husk-based activated carbon (named P95-AC)	Specific surface area = 1543 m ² /g	Rhodamine-B	10 g/l	300 mg/l	360 min	19.8 °C	1.3–10.2	220 mg/g	[59]
47	Treated rice husk-based activated carbon (named PK-AC)	Specific surface area = 1803 m ² /g	Rhodamine-B	10 g/l	300 mg/l	180 min	19.8 °C	1.3–10.2	235 mg/g	[59]
48	Treated rice husk-based activated carbon (named K-AC)	Specific surface area = 2516 m ² /g	Rhodamine-B	10 g/l	300 mg/l	300 min	19.8 °C	1.3–10.2	290 mg/g	[59]
49	White ash	Specific surface area = 236.4 m ² /g	Direct red 28	-	-	-	-	-	171.0 mg/g	[66]
50	White rice husk ash (WRHA)	-	Brilliant green	1 g/l	100 mg/l	30 min	46.8 °C	4–10	66 mg/g	[60]

289.0 mg/g which is about 6.5 times higher than that of the unmodified biomass. Furthermore, authors showed that the adsorbent was used to remove Cu(II) from electroplating wastewater and it was suitable for repeated use for more than four cycles. In their study, orange peel modified with different chemical reagents as biosorbents were used to remove cadmium ion from aqueous solution [27]. Effects of different chemical modifications on the biosorbent properties including washing, alkali saponification, cross-linking temperature and concentration of cross-linking reagent were investigated. Meanwhile, influence of pH of solution, initial cadmium concentration, shaking time and solid/liquid ratio on the removed of Cd(II) by different chemically modified biosorbents was studied. They concluded highlighting that cadmium ion could be removed by 0.6SCA₈₀ (orange peel modified with 0.6 mol/l citric acid under 80 °C after alkali saponification) biosorbent effective and quick. Furthermore, they produced a series of biosorbents with the following order of cadmium: 0.6SCA₈₀ > SOP > CA2 > CA1 > PA1 > PA2 > OP. For 0.6SCA₈₀, the maximum capacity of cadmium was 0.90 mol/kg, the optimum pH value was 6, the reaction balance was established after shaking 120 min and the optimum solid/liquid ratio was 4.3 g/l. The desorption rate of cadmium was 94% with 0.15 mol/l HCl solution. Pandey et al. [72] studied the adsorption of Cd(II) ions from aqueous solutions by modified *Cucumis sativus* peel (CSP) by HCl treatment. The optimum pH, adsorbent mass, contact time, and initial ion concentration were determined. The maximum removal efficiency was 84.85% for 20 mg/l Cd(II) ion at pH 5. Furthermore, the adsorption isotherms were obtained using concentrations of the metal ions ranging from 5 to 150 mg/l.

Lentil husk was found to be a promising low cost adsorbent for removal of lead [73]. The functional groups of lentil husk were modified by treating with different chemicals to investigate their role in adsorption (Formaldehyde-formic acid treatment, Triethyl phosphite–nitromethane treatment, Methanol–hydrochloric acid treatment and acetic anhydride treatment). After modification the biomass was dried and used for adsorption tests. Different physicochemical parameters were found to influence the adsorption process. Lead uptake capacity of lentil husk was 81.43 mg/g at optimized pH (5.0) and temperature (30 °C) with an initial metal ion concentration of 250 mg/l. Furthermore, chemical modification of functional groups revealed both hydroxyl and carboxyl groups played crucial role in binding process. Same biosorbent materials labelled RH-2 and RH-3 and obtained from rice husks (RH-1) were successfully developed through fast and facile esterification reactions with hydroxylethylidenediphosphonic acid and nitriilotrimethylenetriphosphonic acid, respectively [61]. Results revealed that the adsorption property of functionalized rice husks with organotriphosphonic acid RH-3 for Au(III) was very excellent, especially for gold ions. The maximum adsorption capacity could reach 3.25 ± 0.07 mmol/g that is higher than other reported adsorbents. Thus, authors recommend organomultiphosphonated rice husks as potentially low-cost biosorbents with high efficiency for water purification and specious metals uptake. The removal of Cu(II) by adsorption on pomelo peel (PP) and depectinated pomelo peel (DPP) were studied by Tasaso et al. [29]. It was found that the highest Cu(II) adsorption capacity for PP and DPP were 19.7 mg/g and 21.1 mg/g at the following conditions: pH = 4, 125 mg/l of initial concentration, temperature of 25 °C and equilibrium time about 60 min.

Table 3 synthesize the main characteristics of sorbents as well as their adsorption capacities with reference to agriculture and household waste applied for the removal of heavy metals.

Table 3 shows how specific surface area was for 61.5%, 15.4%, 15.4%, 0% and 7.7% in the range of 0–10, 11–100, 101–500, 501–1000 and >1000 m²/g, respectively. Compared to the case of Table 2, specific surface areas are much lower. However, it should be noted how the surface is known only in 19.7% of cases reported in the Table 3 showing an incomplete information [4]. Adsorbent dose are in the range 0.5–40 g/l. Typical dosage is equal to 5 g/l corresponding to the 35.8% of the investigated cases. Generally, dosages are far greater than in the case of

Table 2. Instead, temperature varies in the range of 19.8–40 °C. On 60 available data, only 10% refer to hot processes conducted at temperature around 40 °C highlighting how the most of the processes were conducted at room temperature. Always in this case, however, the available information is not always complete.

Finally, the most significant experiences related to the use of agriculture and household waste sorbents for the removal of various pollutants (i.e., biorecalcitrant compounds, nitrogen and phosphate compounds) from single compound aqueous solution are described.

Njoku et al. [79] utilized sky fruit husk for the preparation of activated carbon by chemical activation with orthophosphoric acid (H₃PO₄). Batch adsorption processes were carried out in order to evaluate the potentiality of the prepared activated carbon having BET surface area of 1211.57 m²/g for the removal of anionic herbicide bentazon from aqueous solution. The maximum adsorption capacity was found to be 166.67 mg/g. The positive value of enthalpy change confirms that adsorption process was endothermic in nature. Furthermore, they concluded that the adsorbent can provide a further insight into the removal of other pesticides in adsorption system. Yadav et al. [31] investigated about possible use of fruit juice (*Citrus limetta*) residue and rice husk as adsorbents for phosphate removal. Batch experiments were performed to achieve maximal phosphate removal by varying process parameters, like pH, contact time, temperature, adsorbent dose and initial solute concentration. Results showed that O–H, N–O and C–N groups are responsible for phosphate binding process. Furthermore, the maximum removal of phosphate was achieved as 95.85% at 24.85 °C, adsorbent dose 3 g/l and pH 6.0 with acid treated fruit juice residue.

Due to its high adsorption capacity, the use of biochar to capture excess nutrients from wastewater has become a central focus in environmental remediation studies. In the study of Kizito et al. [63], the potential use of biochar in adsorption and removal of ammonium in piggery manure anaerobic digestate slurry was investigated. The maximum NH₄⁺-N adsorption from slurry at 1400 mgN/l was 44.64 ± 0.602 mg/g and 39.8 ± 0.54 mg/g for wood and rice husk biochar, respectively. For both biochars, adsorption increased with increase in contact time, temperature, pH and NH₄⁺-N concentration but it decreased with increase in biochar particle size. Based on the removal amounts, authors concluded that rice husk and wood biochar have potential to adsorb NH₄⁺-N from piggery manure anaerobic digestate slurry, and thus can be used as nutrient filters prior to discharge into water streams.

Table 4 synthesize the main characteristics of sorbents as well as their adsorption capacities with reference to agriculture and household waste applied for the removal of various pollutants from single compound aqueous solutions.

Table 4 shows how the specific surface area is for 0%, 0%, 12.5%, 50.0% and 37.5% in the range of 0–10, 11–100, 101–500, 501–1000 and >1000 m²/g, respectively. However, always in this case, available information is not complete in line with Gautam et al. [4]. Adsorbent dose is in the range 0.8–66.6 g/l with a typical value of about 1 g/l, corresponding to the 42.9% of the investigated cases. However, a dose >3 g/l is observed for the 57.1% of the investigated cases. Temperature varies in the range of 23–35 °C showing how most of the processes have been conducted at room temperature. Finally, the available information is not always complete.

From the case studies shown in the Tables 2, 3 and 4, it is evident that raw material can be modified to develop desirable physicochemical properties such as (i) specific surface area, (ii) pore-size distribution, (iii) pore volume and (iv) presence of surface functional groups. The techniques of modification can be categorized into three broad groups: (i) modification of chemical characteristics; (ii) modification of physical characteristics and; (iii) modification of biological characteristics. Among these three methods, modification with chemical compounds has been more frequently employed to increase the adsorption and hence removal capacity of sorbents [4]. As the agents include

Table 3

Main characteristics and uptake capacities of various agricultural and household waste sorbents for heavy metals removal.

N.	Adsorbent		Adsorption test							References
	Type	Characteristics	Pollutants to be removed	Adsorbent dose	Initial pollutant concentration range	Contact time	Temperature	pH	Amount adsorbed (q_e)	
1	Activated carbon from cassava peels	Specific surface area = 473 m ² /g; mean particle size = 128 μm	Cu(II)	10 g/l	4 mg/l	20–120	39.85 °C	8	8.0 mg/g	[70]
2	Activated carbon from cassava peels	Specific surface area = 473 m ² /g; mean particle size = 128 μm	Pb(II)	10 g/l	5.30 mg/l	20–120	39.85 °C	8	5.8 mg/g	[70]
3	Agave bagasse (HCl)	–	Cd(II)	1 g/l	60 mg/l	–	25 °C	5	12.50 mg/g	[23]
4	Agave bagasse (HCl)	–	Pb(II)	1 g/l	60 mg/l	–	25 °C	5	42.31 mg/g	[23]
5	Agave bagasse (HCl)	–	Zn(II)	1 g/l	60 mg/l	–	25 °C	5	12.40 mg/g	[23]
6	Agave bagasse (HNO ₃)	–	Cd(II)	1 g/l	60 mg/l	–	25 °C	5	13.50 mg/g	[23]
7	Agave bagasse (HNO ₃)	–	Pb(II)	1 g/l	60 mg/l	–	25 °C	5	54.29 mg/g	[23]
8	Agave bagasse (HNO ₃)	–	Zn(II)	1 g/l	60 mg/l	–	25 °C	5	14.43 mg/g	[23]
9	Agave bagasse (NaOH)	–	Cd(II)	1 g/l	60 mg/l	–	25 °C	5	18.32 mg/g	[23]
10	Agave bagasse (NaOH)	–	Pb(II)	1 g/l	60 mg/l	–	25 °C	5	50.12 mg/g	[23]
11	Agave bagasse (NaOH)	–	Zn(II)	1 g/l	60 mg/l	–	25 °C	5	20.54 mg/g	[23]
12	Agave bagasse (raw)	–	Cd(II)	2 g/l	60 mg/l	–	25 °C	5	13.27 mg/g	[23]
13	Agave bagasse (raw)	–	Pb(II)	2 g/l	60 mg/l	–	25 °C	5	35.60 mg/g	[23]
14	Agave bagasse (raw)	–	Zn(II)	2 g/l	60 mg/l	–	25 °C	5	7.84 mg/g	[23]
15	Ash gourd peel powder	Mean particle size = 446 μm; specific surface area = 0.4854 m ² /g	Cr(VI)	6 g/l	75–350 mg/l (125 mg/l, better solution)	40–60	28 °C	1	18.7 mg/g	[71]
16	Banana peel	–	Cd(II)	30 g/l	30–80 mg/l	20	25 °C	3	5.71 mg/g	[50]
17	Banana peel	–	Pb(II)	40 g/l	30–80 mg/l	20	25 °C	5	2.18 mg/g	[50]
18	Barley straw (raw)	–	Cu(II)	1 g/l	0.0001–0.001 mol/l	120	25 °C	6–7	4.64 mg/g	[25]
19	Cashew nut shell (raw)	–	Ni(II)	3 g/l	10–50 mg/l	30	30 °C	5	18.86 mg/g	[26]
20	Chemically modified orange peel	–	Cu(II)	2 g/l	50–500 mg/l	180	30 °C	5	289.0 mg/g	[54]
21	Citric acid barley straw (raw)	–	Cu(II)	1 g/l	0.0001–0.001 mol/L	120	25 °C	6–7	31.71 mg/g	[25]
22	Citric acid modified orange peel	–	Cd(II)	4.3 g/l	0.001–0.005 mol/l	120	–	6	0.90 mol/kg	[27]
23	Depectinated pomelo peel	–	Cu(II)	5 g/l	25–125 mg/l	60	25 °C	4	21.1 mg/g	[29]
24	Egyptian mandarin peel (carbonized)	–	Hg(II)	5 g/l	50–200 mg/l	24 h	19.85 °C	6.02	34.84 mg/g	[30]
25	Egyptian mandarin peel (NaOH treated)	–	Hg(II)	5 g/l	50–200 mg/l	24 h	19.85 °C	6.02	23.26 mg/g	[30]
26	Egyptian mandarin peel (raw)	–	Hg(II)	5 g/l	50–200 mg/l	24 h	19.85 °C	6.02	19.01 mg/g	[30]
27	Garden grass (raw)	Specific surface area = 21.28 m ² /g	Pb(II)	0.5 g/l	1–500 mg/l	–	29.85 °C	–	58.34 mg/g	[32]

(continued on next page)

Table 3 (continued)

N.	Adsorbent		Adsorption test							References
	Type	Characteristics	Pollutants to be removed	Adsorbent dose	Initial pollutant concentration range	Contact time	Temperature	pH	Amount adsorbed (q_e)	
28	Grapefruit peel	–	U(VI)	2 g/l	50–500 mg/l	60–80	24.85 °C	4–6	140.79 mg/g	[34]
29	K ⁺ type orange peel adsorbent	Mean diameter = 58 µm	Cu(II)	5 g/l	10–300 mg/l	120	25 °C	5–5.5	59.77 mg/g	[55]
30	KCl modified orange peel	Mean diameter = 58 µm	Cu(II)	5 g/l	10–300 mg/l	120	25 °C	5–5.5	59.77 mg/g	[56]
31	KCl modified orange peel	Mean diameter = 58 µm	Cd(II)	5 g/l	10–300 mg/l	120	25 °C	5–5.5	125.63 mg/g	[56]
32	KCl modified orange peel	Mean diameter = 58 µm	Pb(II)	5 g/l	10–300 mg/l	120	25 °C	5–5.5	141.84 mg/g	[56]
33	KCl modified orange peel	Mean diameter = 58 µm	Zn(II)	5 g/l	10–300 mg/l	120	25 °C	5–5.5	45.29 mg/g	[56]
34	KCl modified orange peel	Mean diameter = 58 µm	Ni(II)	5 g/l	10–300 mg/l	120	25 °C	5–5.5	49.14 mg/g	[56]
35	Lentil shell (raw)	Specific surface area = 0.19 m ² /g	Cu(II)	10 g/l	25–500 mg/l	180	39.8 °C	6	9.59 mg/g	[36]
36	Mango peel waste	Mean particle size = 0.85–1 mm.	Cu(II)	5 g/l	10–500 mg/l	60	25 °C	5–6	46.09 mg/g	[37]
37	Mango peel waste	–	Ni(II)	5 g/l	10–500 mg/l	60	25 °C	5–6	39.75 mg/g	[37]
38	Mango peel waste	–	Zn(II)	5 g/l	10–500 mg/l	60	25 °C	5–6	28.21 mg/g	[37]
39	Mercurized garlic peel	–	Pb(II)	–	1–200 mg/l	60–120	25 °C	4–7	109.05 mg/g	[33]
40	Mg ²⁺ type orange peel adsorbent	Mean diameter = 62 µm	Cu(II)	5 g/l	10–300 mg/l	120	25 °C	5–5.5	40.37 mg/g	[55]
41	Modified Cucumis sativa peel	Particle density = 0.235; porosity = 0.15%; Moisture content = 13.5%; Ash content = 8.5%	Cd(II)	1 g/l	5–150 mg/l	60	24.85 °C	5	58.14 mg/g	[72]
42	Modified lentil husk	–	Pb(II)	–	100 mg/l	48 min	–	–	47.47 mg/g	[73]
43	Mosambi (<i>Citrus limetta</i>) peel	Mean particle size = 180–160 µm	Cr(VI)	5–50 g/l	200–300 mg/l	120	40 °C	2	250 mg/g	[38]
44	Muskmelon peel	–	Pb(II)	5 g/l	1–5 mmol/l	120	25 °C	4.5	167.8 mg/g	[39]
45	Nano-porous activated neem bark	–	Cu(II)	–	200 mg/l	2 days	–	–	21.23 mg/g	[74]
46	Nano-porous activated neem bark	–	Zn(II)	–	200 mg/l	2 days	–	–	11.9 mg/g	[74]
47	Native garlic peel	–	Pb(II)	–	1–200 mg/l	60–120	25 °C	4–7	51.73 mg/g	[33]
48	Olive stone (raw)	Specific surface area = 0.187 m ² /g	Cu(II)	–	3.0×10^{-4} to 0.15 mol/l	60	20 °C	5.5–6	3.19×10^{-5} mol/g	[43]
49	Olive stone (raw)	Specific surface area = 0.187 m ² /g	Pb(II)	–	3.0×10^{-4} to 0.15 mol/l	60	20 °C	5.5–6	4.47×10^{-5} mol/g	[43]
50	Olive stone (raw)	Specific surface area = 0.187 m ² /g	Ni(II)	–	3.0×10^{-4} to 0.15 mol/l	60	20 °C	5.5–6	3.63×10^{-5} mol/g	[43]
51	Olive stone (raw)	Specific surface area = 0.187 m ² /g	Cd(II)	–	3.0×10^{-4} to 0.15 mol/l	60	20 °C	5.5–6	6.88×10^{-5} mol/g	[43]
52	Organomultiphosphonated rice husk	–	Au(III)	–	–	–	–	–	3.25 mg/g	[61]
53	Pomegranate peel	–	Ni(II)	10 g/l	–	120	25 °C	5.5–6.5	52 mg/g	[75]
54	Pomegranate peel carbon	Mean particle size = 0.075 to 0.104 mm	Fe(II)	1 g/l	10–100 mg/l	40	29 °C	6	18.52 mg/g	[44]
55	Pomelo peel	–	Cu(II)	5 g/l	25–125 mg/l	60	25 °C	4	19.7 mg/g	[29]
56	Ponkan peel	115.3 m ² /g	Pb(II)	2 g/l	15 mmol/l	60	25 °C	5	112.1 mg/g	[53]
57	Potato peels	–	Cu(II)	10 g/l	150–400 mg/l	20	29.85 °C	6	0.3877 mg/g	[45]
58	Rice shell (raw)	Specific surface area = 0.67 m ² /g	Cu(II)	10 g/l	25–500 mg/l	180	39.8 °C	6	2.95 mg/g	[36]
59	Rice straw (raw)	–	Cd(II)	–	25–350 mg/ml	180	25 °C	2–6	13.84 mg/g	[46]
60	Sugarcane bagasse (raw)	–	Hg(I)	5 g/l	76 mg/l	60	30 °C	4	35.71 mg/g	[48]
61	Sulfured orange peel	–	Pb(II)	5 g/l	25–800 mg/l	–	30 °C	5	164.0 mg/g	[57]
62	Sulfured orange peel	–	Zn(II)	5 g/l	25–800 mg/l	–	30 °C	5	80.0 mg/g	[57]
63	Sunflower hull (raw)	Specific surface area = 6.06 m ² /g	Cu(II)	2 g/l	25–200 mg/l	180	30 °C	5	57.14 mg/g	[76]
64	Wheat shell (raw)	Specific surface area = 0.83 m ² /g	Cu(II)	10 g/l	25–500 mg/l	180	39.8 °C	6	17.42 mg/g	[36]
65	Wheat stem (raw)	–	Cd(II)	–	0.1–1.2 mmol/l	60	–	5	0.1032 mmol/g	[77]
66	ZnCl ₂ activated grapefruit peel	1186.2 m ² /g	Pb(II)	10 g/l	100 mg/l	90	30 °C	5.3–6.5	12.73 mg/g	[84]

Table 4
Main characteristics and uptake capacities of various agricultural and household waste sorbents for other pollutants removal.

N.	Adsorbent		Adsorption test						References	
	Type	Characteristics	Pollutants to be removed	Adsorbent dose	Initial pollutant concentration range	Contact time	Temperature	pH		Amount adsorbed (q_e)
<i>Biorecalcitrant compounds</i>										
1	Rice husk ash	–	Phenol	66 g/l	$0-1.0 \times 10^{-4}$	60 min	23 °C	10.0	1.53×10^{-4} mol/g	[62]
2	Rice husk ash	–	1,3-Dihydroxybenzene	66 g/l	$0-1.0 \times 10^{-4}$	60 min	23 °C	10.0	8.07×10^{-5} mol/g	[62]
3	Rice husk ash	–	2-Chlorophenol	66 g/l	$0-2.45 \times 10^{-5}$	60 min	23 °C	10.0	1.63×10^{-6} mol/g	[62]
4	Activated carbon cloth	Specific surface area = 2500 m ² /g	Anionic herbicide bentazon	–	20.9 mg/l	2 days	25 °C	–	151.0 mg/g	[78]
5	Date seed-based activated carbon	Specific surface area = 880.18 m ² /g; average pore diameter = 21.60 Å (mesoporous). 1 Å = 0.1 nm	Anionic herbicide bentazon	0.8 g/l	25–250 mg/l	1 days	30 °C	5.5	86.26 mg/g	[85]
6	Banana stalks activated carbon	Particle size range of 0.5–2.0 mm	Anionic herbicide bentazon	1.2 g/l	250 mg/l	1 days	30 °C	–	100.95 mg/g	[86]
7	Branches of pomegranates trees activated carbon	Particle size range of 1–3 mm	Anionic herbicide bentazon	1.5 g/l	200–250 mg/l	8–10 h	30 °C	–	80.0 mg/g	[87]
8	Sky fruit husk activated carbons	Mesoporous (2–50 nm) adsorbent; specific surface area = 1211.57 m ² /g	Anionic herbicide bentazon	0.8 g/l	250 mg/l	20 h	30 °C	5.0	131.11 mg/g	[79]
<i>Nitrogen and phosphate compounds</i>										
9	Activated fruit juice residue	Mean pore radius (μ m) = 0.00194; Specific surface area = 927.3 m ² /g; moisture content = 0.519%; ash = 5.047%.	Phosphate	3.0 g/l	10–30 mg/l	180 min	24.85 °C	6.0–8.0	99.9%	[31]
10	Activated rice husk	Mean pore radius (μ m) = 0.00188; specific surface area = 637.4 m ² /g; moisture content = 0.286%; Ash = 4.8%.	Phosphate	3.0 g/l	10–30 mg/l	180 min	24.85 °C	6.0–8.0	97.0%	[31]
11	Fruit juice residue	–	Phosphate	3.0 g/l	10–30 mg/l	180 min	24.85 °C	6.0–8.0	83.0%	[31]
12	Microwave activated carbonized coconut shells	Particle size range of 1–2 cm; moisture content = 5.64%; ash = 0.63%; specific surface area = 700 m ² /g.	Urea	8 g/l	4959 mg/l; 19,800 mg/l	200 min	30 °C	–	60 mg/g; 256.41 mg/g	[80]
13	Rice husk	–	Phosphate	3.0 g/l	10–30 mg/l	180 min	24.85 °C	6.0–8.0	68.0 mg/g	[31]
14	Rice husk derived biochar	Ash = 41.96%; fixed carbon = 17.34%; specific surface area = 10.955 m ² /g.	Ammonium nitrogen	1.0 g/l	1400 mgN/l	20 h	35 °C	7.0	39.8 mg/g	[63]
15	Wood derived biochar	Ash = 5.87%; Fixed carbon = 80.2%; specific surface area = 273.623 m ² /g.	Ammonium nitrogen	1.0 g/l	1400 mgN/l	20 h	35 °C	7.0	44.64 mg/g	[63]

organic and mineral acids (HCl, HNO₃, H₂SO₄, acetic acid, citric acid and formic acid), bases and basic solutions (NaOH, Na₂CO₃, Ca(OH)₂ and CaCl₂), oxidizing agents (H₂O₂ and K₂MnO₄) and many other mineral and organic chemical compounds (formaldehyde, glutaraldehyde, CH₃OH, polyethyleneimine and epichlorohydrin).

3.2. Industrial waste

Today, industrial activities generate huge amount of solid waste materials as by-products. While some of these are reused others are sent for disposal in landfills. Therefore, the possibility of reuse in adsorption processes represent an interesting solution mainly because these industrial waste material are available almost free of cost and causes major disposal problem. In recent years, a number of industrial wastes have been investigated with or without treatment as adsorbents for the removal of pollutants from wastewaters as well described in Bhatnagar and Sillanpaa [15]. Generally, industrial waste can be divided into the following groups: (i) Fly ash; (ii) Steel industry wastes; (iii) Aluminium industry wastes; (iv) Fertilizer industry waste; (v) Other industry waste such as those from leather industry and paper industry. Fly ash is a waste material originating in combustion processes. The main uses of fly ash include construction of roads, bricks, cement, etc. The high percentage of silica and alumina in fly ash make it a good candidate for utilization as an inexpensive adsorbent for bulk use [15]. Among the steel industry wastes, blast furnace slag, sludge and dust are the most investigated with reference to their applicability in adsorption processes. Considering the aluminium industry wastes, red mud is among the most investigated. Red mud is a waste material formed during the production of alumina when the bauxite ore is subjected to caustic leaching [88]. The toxicity and colloidal nature of red mud particles create a serious pollution hazard. There have been many proposals for the red mud utilization such as in the manufacture of red mud bricks, as filler in asphalt road construction, as iron ore, and as a source of various minerals [5]. After pre-treatment, red mud is suitable for the treatment of wastewaters above all with reference to the treatment of Congo red from aqueous solutions [88]. Instead, fertilizer industry also produces a number of by-products in large quantities which create serious disposal problems and degrade the surrounding environment.

Taking into account the groups mentioned above, the main experiences related to the application of industrial by-products for dyes removal from single compound aqueous solutions are discussed.

Okada et al. [89] investigated the adsorption properties of activated carbons prepared from waste newspaper by chemical and physical activation using methylene blue (MB) as adsorbate. They obtained that the amounts of the functional groups in the surface of the activated carbons were found from XPS data to be higher in the chemically activated products than in the physically activated product. MB adsorption was found to be higher in the chemically activated products than in the physically activated product and commercial carbon samples. This higher MB adsorption is thought to be a function of pore size and hydrophilic surface properties. Tsai et al. [90] demonstrated that the beer brewery waste mostly consisting of diatomite could be directly used as a porous adsorbent based on its pore properties, SEM observations, elemental analyses and adsorption properties. The results showed that the pore properties of adsorbent were higher than those of its precursor diatomite, which was also consistent with the measured adsorption capacities of methylene blue (one of basic dyes) at the equilibrium conditions and the results in the applicability for treating industrial wastewater containing basic dye. Jain et al. [91] investigated a number of low-cost adsorbents from steel and fertilizer industries wastes for the removal of anionic dyes such as ethyl orange, metanil yellow and acid blue 113 from aqueous solutions. The results indicate that inorganic wastes such as blast furnace dust, sludge and slag from steel plants are not suitable for the removal of organic materials, whereas a carbonaceous adsorbent prepared from carbon slurry of fertilizer industry was

found to adsorb 198, 211 and 219 mg/g of ethyl orange, metanil yellow and acid blue 113, respectively. Furthermore, the adsorption data on carbonaceous adsorbent was compared to a standard activated charcoal sample and it was found that the prepared adsorbent is about 80% as efficient as standard activated charcoal and therefore, can be used as low cost alternative (~US\$ 100 per ton) for color removal from effluents. In other studies, Jain et al. [92] used blast furnace dust, sludge and slag from steel plants for the treatment of additional pollutants such as ghrisoidine G, crystal violet and meldola blue. The adsorption of these three basic dyes was studied on all the adsorbents and the results indicated that only carbonaceous adsorbent removed the dyes from solution to an appreciable extent compared to the others. According to Jain et al. [91,92], the carbonaceous adsorbent was prepared from the carbon slurry, generated in national fertilizer plants in India using fuel oil and low sulfur heavy stock. This slurry was dumped in large tanks and allowed to dry. The dried cake material, after powdered, was found to consist of small, black and greasy granules. It was treated with hydrogen peroxide to oxidize the adhering organic material and then washed with distilled water and heated at 200 °C until the evolution of black soot stopped. Subsequently, this material was activated at different temperatures in a muffle furnace for 1 h in air atmosphere. After the activation, the material was treated with 1 M HCl to remove the ash content and washed with distilled water and then dried (yield, 90%) obtaining, finally, the so-called carbonaceous adsorbent. It was sieved to get different mesh sizes and kept in a desiccator.

Janos et al. [93] tested the brown coal fly ashes as potentially low-cost sorbents for the removal of synthetic dyes from waters. It was shown that both basic (cationic) and acid (anionic) dyes can be sorbed onto the fly ash. The sorption capacities were in the range of 10⁻¹–10⁻³ mmol/g and did not differ significantly for basic and acid dyes. The dye sorption decreased in the presence of organic solvents such as methanol and acetone. The presence of oppositely charged surfactants exhibited a pronounced effect on the dye sorption—low concentrations of the surfactant enhanced sorption, whereas high concentrations solubilized the dyes and kept them in solution. Inorganic salts exhibited only a minor effect on the dye sorption. The sorption of basic dyes increased at high pH values, whereas the opposite was true for acid dyes. Lin et al. [94] investigated the use of fly ash treated by H₂SO₄ for the removal of methylene blue from aqueous solution. The raw fly ash was in the form of spherical grayish particles with bulk density of 980 g/L and average particle size of 25 μm. This material was treated with 1 mol/l of H₂SO₄ solution at 50 °C for 24 h. The sample was then washed several times with distilled water, filtrated, dried at 105 °C for 20 h, and sieved to the particle sizes through 450–700 mesh. Results highlighted how the H₂SO₄ treatment increases the specific surface area and pore volume, while decreases its average pore diameter. Further, the adsorption capacity of the fly ash enhances with increasing pH value in basic solution. Wang et al. [95] investigated the use of fly ash and unburned carbon (separated from fly ash) for dye adsorption in methylene blue-containing wastewater. It is found that the unburned carbon exhibits a much higher adsorption capacity than raw fly ash. The adsorption capacities of fly ash and unburned carbon were 2 × 10⁻⁵ and 2.5 × 10⁻⁴ mol/g, respectively. In the experiments, fly ash was obtained from a power station in Western Australia. The bulk chemistry of the raw fly ash was SiO₂ (55%), Al₂O₃ (29%), Fe₂O₃ (8.8%), CaO (1.6%), and MgO (1.0%). To obtain the unburned carbon from fly ash, authors separated the raw fly ash using a physical sieving method to get a carbon-rich sample and then used a sink–float separation method with water to prepare a higher concentrated unburned carbon sample.

Table 5 synthesizes the main characteristics of sorbents as well as their adsorption capacities with reference to industrial waste applied for the removal of dyes from single compound aqueous solutions.

It is possible to observe how the specific surface area is for 31.3%, 43.8%, 18.8%, 3.1% and 3.1% in the range of 0–10, 11–100, 101–500, 501–1000 and > 1000 m²/g, respectively. Adsorbent dose is in the range 0.05–8 g/l with a typical value of 1 g/l, corresponding to 66.6% of the

Table 5
Main characteristics and uptake capacities of various industrial sorbents for dyes removal.

N.	Adsorbent		Adsorption test							References
	Type	Characteristics	Pollutants to be removed	Adsorbent dose	Initial pollutant concentration range	Contact time	Temperature	pH	Amount adsorbed (q_e)	
1	AC-waste newspaper (K900)	Specific surface area = 1740 m ² /g	Basic blue 9	–	–	120 min	–	–	390 mg/g	[89]
2	Beer brewery waste	Specific surface area = 4.5 m ² /g	Basic blue 9	0.25 g/l	2.5 mg/l	24 h	24.85 °C	7.0	4.92 mg/g	[90]
3	Blast furnace sludge	Specific surface area = 28 m ² /g; loss of ignition = 40.5%; SiO ₂ = 12.7%, 200–250 mesh size particles.	Acid blue 113	1 g/l	5.0 × 10 ⁻⁴ M	180 min	25 °C	7.0	2.1 mg/g	[91]
4	Blast furnace sludge	Specific surface area = 28 m ² /g; loss of ignition = 40.5%; SiO ₂ = 12.7%, 200–250 mesh size particles.	Acid yellow 36 (Metanil yellow)	1 g/l	5.0 × 10 ⁻⁴ M	180 min	25 °C	7.0	1.4 mg/g	[91]
5	Blast furnace sludge	Specific surface area = 28 m ² /g; loss of ignition = 40.5%; SiO ₂ = 12.7%, 200–250 mesh size particles.	Ethyl orange	1 g/l	5.0 × 10 ⁻⁴ M	180 min	25 °C	7.0	1.3 mg/g	[91]
6	Blast furnace sludge	Specific surface area = 28 m ² /g; loss of ignition = 40.5%; SiO ₂ = 12.7%, 200–250 mesh size particles.	Basic blue 6 (Meldola's blue)	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5	67 mg/g	[92]
7	Blast furnace dust	Specific surface area = 13 m ² /g; loss of ignition = 24.6%; SiO ₂ = 15.8%, 200–250 mesh size particles.	Basic blue 6	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5	34 mg/g	[92]
8	Blast furnace slag	Specific surface area = 4 m ² /g; loss of ignition = 0.6%; SiO ₂ = 32.7%, 200–250 mesh size particles.	Basic blue 6	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5	3.7 mg/g	[92]
9	Blast furnace sludge	Specific surface area = 28 m ² /g; loss of ignition = 40.5%; SiO ₂ = 12.7%, 200–250 mesh size particles.	Basic blue 6	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5–7.5	6.4 mg/g	[96]
10	Blast furnace dust	Specific surface area = 13 m ² /g; loss of ignition = 24.6%; SiO ₂ = 15.8%, 200–250 mesh size particles.	Basic blue 6	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5–7.5	3.3 mg/g	[96]
11	Blast furnace slag	Specific surface area = 4 m ² /g; loss of ignition = 0.6%; SiO ₂ = 32.7%, 200–250 mesh size particles.	Basic blue 6	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5–7.5	2.1 mg/g	[96]
12	Blast furnace sludge	Specific surface area = 28 m ² /g; loss of ignition = 40.5%; SiO ₂ = 12.7%, 200–250 mesh size particles.	Basic orange 2 (Chrysoidine G)	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5–7.5	10.1 mg/g	[92]

(continued on next page)

Table 5 (continued)

N.	Adsorbent		Adsorption test							References
	Type	Characteristics	Pollutants to be removed	Adsorbent dose	Initial pollutant concentration range	Contact time	Temperature	pH	Amount adsorbed (q_e)	
13	Blast furnace dust	Specific surface area = 13 m ² /g; loss of ignition = 24.6%; SiO ₂ = 15.8%, 200–250 mesh size particles.	Basic orange 2	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5–7.5	5.4 mg/g	[92]
14	Blast furnace slag	Specific surface area = 4 m ² /g; loss of ignition = 0.6%; SiO ₂ = 32.7%, 200–250 mesh size particles.	Basic orange 2	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5–7.5	1.9 mg/g	[92]
15	Blast furnace sludge	Specific surface area = 28 m ² /g; loss of ignition = 40.5%; SiO ₂ = 12.7%, 200–250 mesh size particles.	Basic violet 3 (Crystal violet)	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5–7.5	25.0 mg/g	[92]
16	Blast furnace dust	Specific surface area = 13 m ² /g; loss of ignition = 24.6%; SiO ₂ = 15.8%, 200–250 mesh size particles.	Basic violet 3	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5–7.5	11.0 mg/g	[92]
17	Blast furnace slag	Specific surface area = 4 m ² /g; loss of ignition = 0.6%; SiO ₂ = 32.7%, 200–250 mesh size particles.	Basic violet 3	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5–7.5	3.0 mg/g	[92]
18	Carbonaceous adsorbent prepared from carbon slurry of fertilizer industry	Specific surface area = 380 m ² /g; 200–250 mesh size particles.	Acid yellow 36	1 g/l	3.6–6.0 × 10 ⁻⁴ M	180 min	25 °C	7.0	211.0 mg/g	[91]
19	Carbonaceous adsorbent prepared from carbon slurry of fertilizer industry	Specific surface area = 380 m ² /g; 200–250 mesh size particles	Ethyl orange	1 g/l	3.6–6.0 × 10 ⁻⁴ M	180 min	25 °C	7.0	198.0 mg/g	[91]
20	Carbonaceous adsorbent prepared from carbon slurry of fertilizer industry	Specific surface area = 380 m ² /g; 200–250 mesh size particles	Basic blue 6	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5	170 mg/g	[92]
21	Carbonaceous adsorbent prepared from carbon slurry of fertilizer industry	Specific surface area = 380 m ² /g; 200–250 mesh size particles	Basic blue 9	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5–7.5	92 mg/g	[96]
22	Carbonaceous adsorbent	Specific surface area = 629 m ² /g	Basic green 4	–	1.0 × 10 ⁻⁴ – 1.0 × 10 ⁻³ M	6–8 h	–	–	75.08 mg/g	[97]
23	Carbonaceous adsorbent prepared from carbon slurry of fertilizer industry	Specific surface area = 380 m ² /g	Basic orange 2	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5–7.5	75.0 mg/g	[92]
24	Carbonaceous adsorbent prepared from carbon slurry of fertilizer industry	Specific surface area = 380 m ² /g	Basic violet 3	1 g/l	5.0 × 10 ⁻⁴ M	120 min	25 °C	6.5–7.5	161 mg/g	[92]
25	Fly ash-Czech Republic	Specific surface area = 5.47 m ² /g	Acid red 1	8 g/l	0.05–0.20 mmol/l	72 h	22 °C	3.0–4.5	0.1405 mmol/g	[93]
26	Fly ash-Czech Republic	Specific surface area = 5.47 m ² /g	Acid yellow 11	8 g/l	0.05–0.20 mmol/l	72 h	22 °C	4.0	0.0052 mmol/g	[93]
27	Fly ash-Slovakia	Specific surface area = 3.26 m ² /g	Basic blue 9	8 g/l	0.05–0.20 mmol/l	72 h	22 °C	9.0–10.0	0.0046 mmol/g	[93]
28	Fly ash (treated with H ₂ SO ₄)	Particle sizes range of 450–700 mesh; specific surface area = 6.236 m ² /g;	Basic blue 9	8 g/l	2.675 × 10 ⁻⁵ – 26.75 × 10 ⁻⁵ M	72 h	15 °C	2.5–5.0	0.0021 mmol/g	[94]
29	Fly ash	Specific surface area = 15.6 m ² /g	Basic blue 9	0.025–0.05 g/l	1.0 × 10 ⁻⁶ – 1.0 × 10 ⁻⁵ M	100 h	30 °C	9.0	2.0 × 10 ⁻⁵ mol/g	[95]
30	Fly ash-Slovakia	Specific surface area = 3.26 m ² /g	Basic violet 10	8 g/l	0.05–0.20 mmol/l	72 h	22 °C	–	0.0040 mmol/g	[93]
31	Fly ash-Czech Republic	Specific surface area = 5.47 m ² /g	Basic violet 10	8 g/l	0.05–0.20 mmol/l	72 h	22 °C	–	0.0015 mmol/g	[93]
32	Unburned carbon	Specific surface area = 224.0 m ² /g	Basic blue 9	0.025–0.05 g/l	1.0 × 10 ⁻⁶ – 1.0 × 10 ⁻⁵ M	400 h	30 °C	9.0	2.5 × 10 ⁻⁴ mol/g	[95]

investigated cases. Temperature varies in the range of 15–30 °C highlighting how all the processes were conducted at room temperature. Unlike to the case of Tables 2, 3 and 4, the available information is quite complete. The most significant experiences related to the use of industrial waste sorbents for the removal of heavy metals from single compound aqueous solution are described here. Gupta [98] investigated the use of activated slag developed from blast furnace waste material for the removal of copper and nickel. The waste was washed with distilled water to remove the adhering impurities and dried at 200 °C. The heated product was cooled and activated in air in a Muffle furnace at 600 °C for 1 h. The product was sieved before use to obtain a desired particle size such as 100–150, 150–200, and 200–250 B.S.S. mesh. The studies were carried out with the slag of particle diameter 0.089 mm (mesh 150–200) unless stated otherwise. Finally, it was stored in a desiccator until used. The results show that the waste material can be fruitfully employed for the removal of Cu(II) and Ni(II) in a wide range of concentrations. Furthermore, the column studies indicated that the product can be used on an industrial scale as well. It could be possible to quantitatively recover Ni(II) by 1% HNO₃, and the product has successfully been used for the removal of Ni(II) and Cu(II) from an effluent of a metal finishing plant.

Adsorption removal of Cu(II) from aqueous solution by basic oxygen furnace slag (BOFs) which was activated by the mechanochemistry process was investigated by Xue et al. [99]. BOFs adsorbents were prepared by vertical planetary ball milling and moderate ball milling, and characterized by SEM and XRD. Batch experiments were performed to evaluate the influences of various experimental parameters like the initial concentration of adsorbate, pH value, contact time, and temperature on the removal of Cu(II). Results showed that in a low concentration solution, the optimum condition for removal was found to be 0.5 g adsorbent on the treatment of 1000 mg/l adsorbate. The Cu(II) removal rate could reach 99.9% by the precipitation and adsorption effect. Furthermore, the initial concentration of solution was the most important factor to influence the Cu(II) removal, while temperature showed negligible effect due to the existence of precipitation. Hence, initial concentration and pH value should be preferentially considered for the heavy metal removal from solution by such alkaline adsorbent.

Lignin extracted from black liquor – a paper industry waste material, was characterized and used for the removal of lead and zinc metals [100]. Black liquor was acidified with dilute HCl till the precipitation was complete. The precipitate was then allowed to settle and centrifuged at 4500 rpm, washed repeatedly with distilled water to remove chloride ions, then dried and stored in a vacuum desiccator. The product was purified by preparing a 10% w/w solution of lignin in dioxane and then adding it dropwise from a burette into vigorously stirred anhydrous ether, to precipitate lignin again. The precipitate was filtered and washed immediately with ether and then benzene, and finally with low boiling petroleum ether, then dried over anhydrous calcium chloride under vacuum. The uptake of lead was found to be greater than the uptake of zinc, and the sorption capacity increases with increasing pH. Kanel et al. [101] tested blast furnace slag (BFS) for the removal of As(III), which is a highly toxic, mobile and predominant species in anoxic groundwater. The dried BFS was treated with hydrogen peroxide at 60 °C for 24 h to oxidize the adhering organic matter before use. After grounding, it was washed with distilled water to remove fine particles, and was dried at 100 °C for 12 h. Subsequently, it was screened to get different geometrical sizes of 0 to 75, 75 to 180, 180 to 425, 425 to 600 and 600 to 1700 µm for the adsorption study. Authors have also investigated the effects of competing anions in the As(III) adsorption process. The obtained results showed that showed HCO₃⁻, NO₃⁻, SO₄²⁻, H₄SiO₄⁰ and PO₄³⁻ (>10 mM) are potential interferences in the As(III) adsorption reaction. When the concentration of anions was increased further up to 10 mM, the adsorption of As(III) on BFS decreased from 99.9 to 74.8, 44.6, 42.2, 30.0 and 10.0% for nitrate, sulfate, bicarbonate, silicate and phosphate ions, respectively. Bibi et al. [104] aimed to assess selected industrial waste materials for

simultaneous removal of arsenic and fluoride from drinking water in order to find cost effective adsorbent. Commercially available Hydrated Cement, Marble Powder (waste) and Brick Powder (waste) were used. Removal percentage of studied adsorbents followed the decreasing trend: Hydrated Cement > Bricks Powder > Marble Powder. All the adsorbents (Hydrated Cement, Bricks Powder and Marble Powder) showed removal % >90 for arsenic and >75% for fluoride from an aqueous solution of 1000 mg/l of As and 30 mg/l of fluoride at pH 7.0 and 8, with the contact period of 60 min and a dose of 30 g/l. Furthermore, other ions did not greatly affect the adsorption of arsenic thereby indicating that these adsorbents were selective adsorbent for arsenic. Hegazi et al. [107] investigated the possibility of use fly ash in adsorption processes for the removal of various heavy metals such as Fe, Pb, Ni, Cd and Cu. Results showed that low cost adsorbents can be fruitfully used for the removal of heavy metals with a concentration range of 20–60 mg/l. Still, using real wastewater, they showed that rice husk was effective in the simultaneous removal of Fe, Pb and Ni, where fly ash was effective in the removal of Cd and Cu.

Fathima et al. [108] investigated the use of waste of the leather processing industry in adsorption processes. In particular, they considered fleshing from animal hides/skins, high in protein content. Raw fleshing was complexed with iron and used for removal of chromium (VI) according to the following points. The raw fleshing was washed well to remove either loosely adhering debris such as hair, blood, dung, etc. The fleshing was dehydrated gradually using an acetone-water mixture. The dehydrated fleshing was then dried in a vacuum drier and finally ground into fine powder (mesh size 3 mm), which was used for further studies. One volume of flesh powder was soaked in three volumes of water for 12 h. Subsequently, the water-saturated flesh powder was drained of excess fluid and treated with an equal weight of 2% ferric chloride at pH 3.0 in a mechanical shaker for 4 h. The final pH of the solution was adjusted to 4.0 using sodium bicarbonate. After treatment, the fleshing particles were rinsed to remove any unfixed iron and stored in an airtight container to avoid change in moisture content. Iron treatment is shown to greatly improve adsorption of the fleshing for hexavalent chromium. The ultimate adsorption capacity of iron treated fleshing is 51 mg of chromium-(VI) per gram of fleshing. That of untreated fleshing is 9 mg/g such that iron treatment increases the adsorption capacity of fleshing by 10-fold.

Red mud has been converted into an inexpensive and efficient adsorbent and used for the removal of lead and chromium from aqueous solutions [110]. Effect of various factors on the removal of these metal ions from water (i.e., pH, adsorbent dose, adsorbate concentration, temperature, particle size, etc.) as well as those related to the presence of other metal ions/surfactants on the removal of Pb(II) and Cr(VI) were studied. Red mud was at first treated with hydrogen peroxide at room temperature for 24 h to oxidize the adhering organic impurities and then washed repeatedly with doubly distilled water. The resulting product was dried at 100 °C cooled and again activated in air in a Muffle furnace at 500 °C for 3 h. The activated red mud was crushed to smaller particles and sieved to desired particle size. The studies were carried out with the red mud of particle diameter (150 ± 200 B.S.S. mesh or 0.089 mm). Finally, the product was stored in a vacuum desiccator until used. Results showed that the uptake of chromium is more than that of lead and is comparable to other commercially available adsorbents. The results indicate that the red mud can be successfully employed for the removal of Pb(II) and Cr(VI) in a wide range of concentrations.

Table 6 summarizes the main characteristics of sorbents as well as their adsorption capacities with reference to industrial waste applied for the removal of heavy metals from single compound aqueous solutions.

It is possible to observe how the specific surface area is for 10.5%, 68.4%, 10, 5%, 0% e 10.5% in the range of 0–10, 11–100, 101–500, 501–1000 and >1000 m²/g, respectively. Adsorbent dose is in the range 0.06–50 g/l. For 56% of the investigated cases, the dose is >1 g/l.

Table 6
Main characteristics and uptake capacities of various industrial sorbents for heavy metals removal.

N.	Adsorbent		Adsorption test							References
	Type	Characteristics	Pollutants to be removed	Adsorbent dose	Initial pollutant concentration range	Contact time	Temperature	pH	Amount adsorbed (q_e)	
1	Activated slag	Specific surface area = 107 m ² /g. Particle size = particle diameter 0.089 nm (150–200 mesh)	Cu(II)	20 g/l	1.57×10^{-3} M	24 h	30 °C	5	30.0 mg/l	[98]
2	Activated slag	Specific surface area = 107 m ² /g. Particle size = particle diameter 0.089 nm (150–200 mesh)	Ni(II)	10 g/l	4.25×10^{-3} M	24 h	30 °C	5	29.35 mg/l	[98]
3	Basic oxygen furnace slag	Size fraction <0.6 mm	Cu(II)	0.5 g/l	1200 mg/l	120 min	20 °C	6–8	380.0 mg/g	[99]
4	Black liquor	Specific surface area = 1440 m ² /g	Pb(II)	2–6 g/l	0.97×10^{-4} - 9.7×10^{-4} M	24 h	30 °C	4–6	18.65 mg/g	[100]
5	Black liquor	Specific surface area = 1440 m ² /g	Zn(II)	2–6 g/l	1×10^{-5} - 1×10^{-4} M	24 h	30 °C	5–7	95.0 mg/g	[100]
6	Blast furnace slag	Specific surface area = 12.56 m ² /g	As(III)	10 g/l	1 mg/l	72 h	25 °C	12	1.40 mg/g	[101]
7	Blast furnace slag	Specific surface area = 107 m ² /g. Particle size = particle diameter 0.089 nm (150–200 mesh)	Zn(II)	20 g/l	1.52×10^{-3} M	–	30 °C	6	17.66 mg/g	[102]
8	Blast furnace slag	Specific surface area = 107 m ² /g. Particle size = particle diameter 0.089 nm (150–200 mesh)	Cd(II)	10 g/l	8.89×10^{-4} M	–	30 °C	5	18.72 mg/g	[102]
9	Blast furnace sludge	Specific surface area = 27.43 m ² /g	Pb(II)	50 g/l	4000 mg/l	5 h	20 °C	–	64.17–79.87 mg/g	[103]
10	Blast furnace sludge	Specific surface area = 27.43 m ² /g	Cu(II)	50 g/l	2300 mg/l	5 h	20 °C	–	16.07–23.66 mg/g	[103]
11	Blast furnace sludge	Specific surface area = 27.43 m ² /g	Cr(III)	50 g/l	1600 mg/l	5 h	20 °C	–	9.55–16.05 mg/g	[103]
12	Blast furnace sludge	Specific surface area = 27.43 m ² /g	Cd(II)	50 g/l	1500 mg/l	5 h	20 °C	–	6.74–10.15 mg/g	[103]
13	Blast furnace sludge	Specific surface area = 27.43 m ² /g	Zn(II)	50 g/l	1500 mg/l	5 h	20 °C	–	4.25–9.25 mg/g	[103]
14	Bricks Powder	–	As(V)	–	1000 mg/l	60 min	–	–	>90%	[104]
15	Chemical treated Fly ash	Specific surface area = 140 m ² /g	As(V)	2 g/l	50 mg/l	8 h	25 °C	2.5	19.46 mg/g	[105]
16	Fly ash	–	Cu(II)	1 g/l	$1-2 \times 10^{-4}$ M	60	30 °C	6.5	1.39 mg/g	[106]
17	Fly ash	–	Fe(II)	0.06 g/l	11.78 mg/l	120	20 °C	6	86.7%	[107]
18	Fly ash	–	Pb(II)	0.06 g/l	1.17 mg/l	120	20 °C	6–7	76.06%	[107]
19	Fly ash	–	Cd(II)	0.06 g/l	0.48 mg/l	120	20 °C	6–7	73.54%	[107]
20	Fly ash	–	Cu(II)	0.06 g/l	5.43 mg/l	120	20 °C	6	98.54%	[107]
21	Fly ash	–	Ni(II)	0.06 g/l	1.74 mg/l	120	20 °C	7	96.03%	[107]
22	Hydrated Cement	–	As(V)	–	1000 mg/l	60 min	–	–	>90%	[104]
23	Iron complexed leather industry waste	Mesh size 3 mm	Cr(VI)	5 g/l	400 mg/l	180 min	–	4	51.0 mg/g	[108]
24	Marble Powder	–	As(V)	–	1000 mg/l	60 min	–	–	>90%	[104]
25	Red mud	Specific surface area = 58 m ² /g	Cu(II)	1 g/l	0.1–0.6 g/l	48 h	–	5.6–6.2	19.72 mg/g	[109]
26	Red mud	Specific surface area = 58 m ² /g	Zn(II)	1 g/l	0.2–0.7 g/l	48 h	–	6.9–7.8	12.59 mg/g	[109]
27	Red mud	Specific surface area = 58 m ² /g	Ni(II)	1 g/l	0.1–0.75 g/l	48 h	–	7.5–7.9	10.95 mg/g	[109]
28	Red mud	Specific surface area = 58 m ² /g	Cd(II)	1 g/l	0.1–0.75 g/l	48 h	–	4.7–6.2	10.57 mg/g	[109]
29	Red mud	Specific surface area = 108 m ² /g	Pb(II)	10 g/l	$2.41-4.83 \times 10^{-3}$ M	24 h	30 °C	4	64.79 mg/g	[110]
30	Red mud	Specific surface area = 108 m ² /g	Cr(VI)	10 g/l	9.60×10^{-4} - 9.60×10^{-3} M	24 h	30 °C	2	35.66 mg/g	[110]
31	Solid waste from leather industry	Specific surface area = 3 m ² /g	As(V)	–	40–60 mg/l	24 h	25 °C	1	26.4 mg/g	[111]
32	Solid waste from leather industry	Specific surface area = 3 m ² /g	Cr(VI)	–	700 mg/l	24 h	25 °C	1	133.3 mg/g	[111]

Temperature varies in the range 20–30 °C highlighting how all the processes were conducted at room temperature. Furthermore, the available information is not always complete.

Finally, the most significant experiences related to the use of industrial waste sorbents for the removal of various pollutants from single compound aqueous solution are described here. Stellacci et al. [112] enhanced the adsorption characteristics of coal fly ash by means of mechano-chemical activation with a high energy mono-planetary ball mill. The best performing sample for the adsorption of phenol from aqueous solution (i.e., fly ash with the higher carbon content and mechano-chemically activated for 4 h in N₂ atmosphere) was compared with powdered activated carbon, yielding quite encouraging results such as favorable adsorption isotherms, improved specific adsorption capacity and very fast adsorption rate. Furthermore, authors highlighted the possibility to use coal fly ash in other environmental applications such as stabilization/solidification treatment of hazardous waste and contaminated soil. Fuel oil fly ash was tested as low-cost carbon-based adsorbent of 2-chlorophenol (CP), 2-chloroaniline (CA) and methylene blue (MB) from aqueous solutions [113]. Results showed that 2-chlorophenol, 2-chloroaniline and methylene blue can be effectively adsorbed onto fuel oil fly ash. This waste can be employed without any expensive pre-treatment, due to the high fraction of unburned particles. The adsorption capacity against 2-chlorophenol and methylene blue has been found similar to that of other carbon rich waste-based adsorbents. Furthermore, other experiences are summarized in Table 7.

It is possible to observe how the specific surface area is for 25% and 75% in the range of 11–100 and 101–500 m²/g, respectively. Adsorbent dose is in the range 0.2–9.6 g/l even though in the case of fuel oil fly ash dosages are greater as a function of the initial pollutant concentration (around 1–1.5 g/l). Temperature is 25 °C and all the processes were conducted at room temperature. Furthermore, also in this case, available information is not always complete in line with Gautam et al. [4].

3.3. Sludge

In the recent past, several sewage sludge based adsorbents have been used for the removal of pollutants from aqueous solutions as reported in literature [115–117]. Sewage sludge based adsorbents have been produced by different chemical activation methods [118, 119] which were then used for the adsorption of phenols, metals and dyes from wastewaters. Some of them are discussed here. Otero et al. [120] investigated about the potential application of adsorbents produced from sewage sludge in organic pollutants removal. The properties of this type of material were studied by liquid-phase adsorption using crystal violet, indigo carmine and phenol as adsorbates. Sewage sludge collected both from the primary sedimentation and the secondary aerobic biological treatment was later submitted to anaerobic digestion. Adsorbent materials from sewage sludge were produced by chemical activation by H₂SO₄ impregnation followed by pyrolysis. The parent sludges were initially oven dried at 105 °C to constant mass and the dried sludges were then ground to approximately 1 mm in diameter particles. At this stage, chemical activation was undertaken by impregnating the sludges with H₂SO₄ in a 1:1 by mass proportion. Sludge was kept in contact with the acid over 48 h in a continuously mixed reactor. The ensuing activated sludges were then pyrolysed under inert nitrogen, with a heating rate of 40 °C/min up to 625 °C with a dwell time of 30 min at this temperature. After pyrolysis, the particles were washed with dilute HCl (10% by mass) to remove remaining activating agent. Finally, after oven drying at 80 °C, the resultant materials were ground and sieved to obtain particles with a diameter between 0.12 and 0.5 mm. These adsorbent particles were submitted to further grinding to secure a fraction of diameter < 0.12 mm. After chemical activation and pyrolysis treatment, sewage sludge provides materials of great porosity and high specific surface area (390 m²/g for activated sewage sludge and 80.0 m²/g for pyrolysed one). Results

Table 7
Main characteristics and uptake capacities of various industrial sorbents for other pollutants removal.

N.	Adsorbent Type	Characteristics	Adsorption test				References			
			Pollutants to be removed	Adsorbent dose	Initial pollutant concentration range	Contact time		Temperature	pH	Amount adsorbed (q _e)
1	Coal fly ash by mechano-chemical activation (MAFA ₉₀)	Specific surface area = 69 m ² /g; iodine no. = 238 mg/g; volume of micropores = 0.180 ml/g; particle size ≤63 μm.	Phenol	9.6 g/l	200 mg/l	120 min	25 °C	9.0	11.39 mg/g	[112]
2	Fertilizer industrial waste (carbon slurry waste)	Specific surface area = 380 m ² /g (activation temperature of 500 °C)	4-bromophenol	0.2 g/l	4.10 ⁻⁴ M	480 min	25 °C	5.5–6.5	40.7 mg/g	[114]
3	Fertilizer industrial waste (carbon slurry waste)	Specific surface area = 380 m ² /g (activation temperature of 500 °C)	2-bromophenol	0.2 g/l	4.10 ⁻⁴ M	480 min	25 °C	5.5–6.5	170.4 mg/g	[114]
4	Fertilizer industrial waste (carbon slurry waste)	Specific surface area = 380 m ² /g (activation temperature of 500 °C)	2,4-dibromophenol	0.2 g/l	4.10 ⁻⁴ M	480 min	25 °C	5.5–6.5	190.2 mg/g	[114]
5	Fuel oil fly ash	Particle size max = 180 μm; LOI (Loss of ignition) = 54.4%; SiO ₂ = 15.0%; Al ₂ O ₃ = 16.2%	2-chlorophenol	0.80–200 g/l	1.5 g/l	120 min	25 °C	6.65–7.70	70.0 mg/g	[113]
6	Fuel oil fly ash	Particle size max = 180 μm; LOI (Loss of ignition) = 54.4%; SiO ₂ = 15.0%; Al ₂ O ₃ = 16.2%	2-chloroaniline	0.80–200 g/l	1 g/l	120 min	25 °C	7.00–7.77	36.0 mg/g	[113]

showed that the sludge-derived activated carbon could adsorb the three adsorbates considered with the time required to reach equilibrium and full adsorptive capacity varying between the adsorbates. Crystal violet adsorption was higher and faster than indigo carmine or phenol. Rio et al. [121] optimized the conditions for sorbents preparation from sewage sludge using experimental design methodology. Series of carbonaceous sorbents were prepared by chemical activation with sulfuric acid. The sorbents produced were characterized, and their properties (surface chemistry, porous and adsorptive properties) were analyzed as a function of the experimental conditions (impregnation ratio, activation temperature and time). Carbonaceous sorbents developed from sludge allow copper ion, phenol and dyes (Acid Red 18 and Basic Violet 4) to be removed from aqueous solution. According to experimental conditions, copper adsorption capacity varies from 77 to 83 mg/g while phenol adsorption capacity varies between 41 and 53 mg/g. Furthermore, in order to have a high mass yield and to minimize the energetic cost of the process, the following optimal conditions, 1.5 g of H_2SO_4/g of sludge, 700 °C and 145 min are more appropriate for use of activated carbon from sludge in water treatments.

Wine processing waste sludge has been shown to be an effective adsorbent for the adsorption of Cr(III) from aqueous solution as reported in Li et al. [122]. The sludge, produced from the final clarifier and coagulation settling basin of the wastewater treatment plant of the wine-processing factory, was washed with deionized water to remove easily suspended materials and dried at 105 °C for 24 h. The dehydration sludge was sieved into three particle size ranges, 50–100, 100–140, and 140–200 mesh, which were represented as average diameters of 0.297, 0.149, and 0.105 mm, respectively. The prepared sludge was then desiccated and stored in an air-tight container. The specific surface area, the organic, nitrogen and phosphorous content of the sludge were 10 m²/g, 40.5%, 23.4% and 6.9%, respectively. Results showed that wine processing waste sludge can be used as an adsorbent for the effective removal of Cr(III) from aqueous solution. Gupta and Garg [117] examined the performance of sewage sludge based adsorbents or the removal of two recalcitrant pollutants (i.e. lignin and amoxicillin) from synthetic wastewater solutions (adsorbate concentration = 50–250 mg/l). The oven-dried sludge was activated chemically by mixing with ZnCl₂ solution in two different mass ratios (i.e. 1:2 and 1:2.5). The slurry was then subjected to pyrolysis at 600 °C for 1 h. Subsequently, the pyrolysed material was washed with acid and water in the same sequence. The adsorbents were represented as ACZn2 and ACZn2.5 in accordance to the mass ratio of the activating agent to sludge material (i.e., 2 and 2.5, respectively). The specific surface area of ACZn2 and ACZn2.5 adsorbents was 500 and 510.8 m²/g, respectively. Results showed reasonable performance for the removal of lignin and AMX from synthetic wastewater.

Finally, sewage sludge, fish waste, and mixtures of the two were pyrolyzed at 650 and 950 °C in order to convert them into stable adsorbents [123]. To test their performance in the removal of pharmaceuticals from water, sulfamethoxazole (SMX) and trimethoprim (TMP) were chosen as model adsorbates. Adsorption isotherms were measured in batch adsorption tests at room temperature. The adsorbents prepared at 950 °C were more effective than those obtained at 650 °C. Even though both pharmaceuticals were adsorbed in the highest amount on the material composed of pyrolyzed fish waste, for TMP removal the composite obtained from 90% sewage sludge and 10% fish waste was equally effective. Furthermore, authors highlighted how favorable surface chemistry seems to be the factor governing the performance of these adsorbents as media for the pharmaceuticals removal from an aqueous phase. The main adsorption mechanism is based on chelation, acid-base interactions and polar interactions with the inorganic phase.

In this regard, Table 8 summarizes the main characteristics as well as the adsorption capacities of other sludge-based adsorbents.

It is possible to observe how the specific surface area is for 21.1%, 21.1%, 36.8%, 21.1% e 0% in the range of 0–10, 11–100, 101–500, 501–

1000 and >1000 m²/g, respectively. Adsorbent dose is in the range 0.4–40 g/l. For 68.4% of the investigated cases, dose is >2.5 g/l. Temperature varies in the range of 20–30 °C and all the processes were conducted at room temperature. Furthermore, the available information is not always complete in line with Gautam et al. [4].

3.4. Sea materials

Adsorbents based on sea materials include (i) chitosan and seafood processing wastes, (ii) peat moss and (iii) seaweed and algae. Due to its abundance, chitin appears economically attractive as well as environmentally friendly. According to Ali et al. [5], >1362·10⁶ tons/annum of chitin are available from the fisheries of crustaceans. Chitosan, that is in a group of glucosamine (which in turn is a saccharide and unit of chitosan) called polysaccharide, is a deacetylated derivative of chitin and can be chemically prepared from chitin. Chitosan is found in the cell wall of some fungi like *Mucorales* stains and used as an effective adsorbent. Peat is a complex soil material with decomposed organic matter. Lignin and cellulose are major constituents of peat. These constituents, especially lignin, contain polar functional groups that can be involved in chemical bonding. Because of these properties, peat moss tends to have a high cation capacity and can be effectively used as an adsorbent for the removal of a variety of pollutants [5].

Finally, some seaweed such as brown algae have significant ion exchange properties associated with their polysaccharide content. Although seaweed has demonstrated extremely high sorption capacities, Holan et al. [128] observed that the biomass had a tendency to disintegrate and swell, which could be effectively used for column operations. Modifications of seaweeds by cross linking increases the stability and mechanical properties as reported in Ali et al. [5]. Instead, some experiences related to the application of sea materials-based sorbents for pollutants removal from aqueous solutions are herein described. The adsorption in some natural materials containing chitin namely, Squid (*Loligo vulgaris*) and Sepia (*Sepia officinalis*) pens, and Anodonta (*Anodonta cygnea*) shells for color removal from textile wastewaters was studied by Figueiredo et al. [129]. A reactive and a direct green dyestuff, the Cibacron green T3G-E (CI reactive green 12) and the Solophenyl green BLE 155% (CI direct green 26), respectively, were tested. In order to improve the adsorbents performances, the materials were submitted to chemical treatment (demineralization and/or deproteinization). Adsorption batch tests showed that the best results could be achieved after deproteinization of the Squid pen and after demineralization of the other materials. The demineralized materials were obtained after reaction with 10% HCl (10 ml/g material) at room temperature, until neutral (or constant) pH was reached. The deproteinization was performed with 10% NaOH (15 ml/g material) at 75–80 °C, during 6 h. After the chemical treatment the materials were filtered, washed with distilled water and acetone, and finally dried at 40 °C and sieved. Results showed how the chemical treatment increases. Ribeiro et al. [130] studied the physicochemical and morphological characterization of fish scales evaluating, also, their adsorption capacities for the removal of reactive blue 5G (RB5G) from aqueous solution. The fish scales of *O. niloticus* species were used as an adsorbent material. Initially, the fish scales were washed with a solution of sodium hypochlorite (0.1%, v/v) and then with distilled water. Afterwards, the adsorbent was dried at 60 °C (until a constant mass was achieved) and then triturated and sieved in particle of 6, 12, 16, 32, 100, 150 and 325 mesh. A portion of adsorbent was treated with HCl aqueous solution (0.1 M). The acid treated adsorbent was prepared by transferring the raw biomass into acid solution and then stirring the mixture at 100 rpm for 24 h at 30 °C. The biomass was washed with distilled water (until a constant pH was achieved) and dried at 60 °C. Thus, two adsorbents were prepared: untreated (ADS) and acid treated (HADS). Results showed that the morphological characterization of the adsorbent presented an average pore size (20.6 Å) characteristic of mesoporous materials. However, based on the very low values of total

Table 8
Main characteristics and uptake capacities of various sludge sorbents for pollutants removal.

N.	Adsorbent		Adsorption test						References
	Type	Characteristics	Pollutants to be removed	Adsorbent dose	Initial pollutant concentration range	Contact time	Temperature	pH	
<i>Dyes</i>									
1	Activated sewage sludge	Specific surface area = 390 m ² /g	Acid blue 74 (Indigo carmine)	5 g/l	100–1000 mg/l	165 min	25 °C	–	60.04 mg/g [120]
2	AC sludge based	Specific surface area = 253 m ² /g; average pore diameter of 2.3 nm.	Acid brown 283	1.6 g/l	30–250 mg/l	120 min	20 °C	3.0–4.0	20.5 mg/g [124]
3	AC sludge based	Specific surface area = 253 m ² /g; average pore diameter of 2.3 nm.	Basic red 46	1.6 g/l	30–250 mg/l	120 min	20 °C	10.0–11.0	188 mg/g [124]
4	Activated sewage sludge	Specific surface area = 390 m ² /g	Basic violet 3 (Crystal violet)	5 g/l	100–1000 mg/l	20 min	25 °C	–	270.8 mg/g [120]
5	AC sludge based	Specific surface area = 253 m ² /g; average pore diameter of 2.3 nm.	Direct red 89	1.6 g/l	30–250 mg/l	120 min	20 °C	2.0–5.0	49.2 mg/g [124]
6	Crude sewage sludge	Specific surface area = 5.28 m ² /g	Vat blue 4	–	–	1 day	25 °C	9.2	248.3 mg/g [125]
7	Crude sewage sludge	Specific surface area = 5.28 m ² /g	Direct red 79	–	–	1 day	25 °C	6.4	19.6 mg/g [125]
8	Pyrolysed sewage sludge	Specific surface area = 80.0 m ² /g	Acid blue 74	5 g/l	100–1000 mg/l	180 min	25 °C	–	30.8 mg/g [120]
9	Pyrolysed sewage sludge	Specific surface area = 80.0 m ² /g	Basic violet 3	5 g/l	100–1000 mg/l	90 min	25 °C	–	184.68 mg/g [120]
<i>Heavy metals</i>									
10	Carbonaceous sorbents from sewage sludge	Particle size = 0.1–1 mm. Specific surface area = 2.9 m ² /g	Cu(II)	0.5 g/l	100 mg/l	–	20 °C	5	77–83 mg/g [121]
11	Crome sludge	Specific density = 1.83	As(V)	40 g/l	400 mg/l	120	–	8.04	22.0 mg/g [126]
12	Distillery sludge	–	Cr(VI)	6–10 g/l	10 mg/l	105	–	3	5.7 mg/g [127]
13	Wine processing waste sludge	Specific surface area = 10 m ² /g	Cr(III)	10 g/l	150 mg/l	120	30 °C	4	70.0% [122]
<i>Other pollutants</i>									
14	Sewage sludge derived adsorbents (ACZn2)	Specific surface area = 500 m ² /g; total pore volume = 0.289 cm ³ /g; carbon (% dry basis) = 62.25; average pore diameter = 4.58 nm	Lignin	2.5 g/l	100 mg/l	–	–	7.0	32.8 mg/g [117]
15	Sewage sludge derived adsorbents (ACZn2.5)	Specific surface area = 510.8 m ² /g; total pore volume = 0.297 cm ³ /g; Carbon (% dry basis) = 69.85; average pore diameter = 4.67 nm	Lignin	2.5 g/l	100 mg/l	–	–	7.0	34 mg/g [117]
16	Sewage sludge derived adsorbents (CAC)	Specific surface area = 514.12 m ² /g; total pore volume = 0.296 cm ³ /g; Carbon (% dry basis) = 92.06; average pore diameter = 4.67 nm	Lignin	2.5 g/l	100 mg/l	–	–	7.0	34.4 mg/g [117]
17	Sewage sludge derived adsorbents (ACZn2)	Specific surface area = 500 m ² /g; total pore volume = 0.289 cm ³ /g; Carbon (% dry basis) = 62.25; average pore diameter = 4.58 nm	Amoxicillin (antibiotic)	2.5 g/l	100 mg/l	–	–	6.0	22.67 mg/g [117]
18	Sewage sludge derived adsorbents (ACZn2.5)	Specific surface area = 510.8 m ² /g; total pore volume = 0.297 cm ³ /g; carbon (% dry basis) = 69.85; average pore diameter = 4.67 nm	Amoxicillin (antibiotic)	2.5 g/l	100 mg/l	–	–	6.0	24 mg/g [117]
19	Sewage sludge derived adsorbents (CAC)	Specific surface area = 514.12 m ² /g; total pore volume = 0.296 cm ³ /g; carbon (% dry basis) = 92.06; average pore diameter = 4.67 nm	Amoxicillin (antibiotic)	2.5 g/l	100 mg/l	–	–	6.0	27 mg/g [117]
20	Sewage sludge and fish waste derived adsorbents	Particle size between 25 and 600 μm; specific surface area = 34 m ² /g at 950 °C (the pyrolysis temperature)	Sulfamethoxazole (SMX) (Pharmaceuticals)	0.4 g/l	0.01–0.4 mmol/l	5 h	30 °C	–	0.02 mg/g [123]
21	Sewage sludge and fish waste derived adsorbents	Particle size between 25 and 600 μm; specific surface area = 34 m ² /g at 950 °C (the pyrolysis temperature)	Trimethoprim (TMP)	0.4 g/l	0.01–0.25 mmol/l	5 h	30 °C	–	0.046 mg/g [123]

pore volume ($0.003 \text{ cm}^3/\text{g}$), the adsorbent was considered a non-porous material. The specific surface area achieved was $2.6 \text{ m}^2/\text{g}$. Still, comparing the RB5G dye uptake at different initial pH values (2, 7, 10), a higher capacity was achieved in acidic medium. The equilibrium adsorption data of RB5G dye at pH 2 showed a maximum capacity of 241.20 mg/g with fast kinetics. Peng et al. [131] prepared novel nanoporous magnetic cellulose–chitosan composite microspheres (NMCMs) by sol–gel transition method using ionic liquids as solvent for the sorption of Cu(II). Briefly, Fe_3O_4 nanoparticles were firstly synthesized by chemical coprecipitation method under alkaline conditions. Cellulose and chitosan were dissolved in 1-Butyl-3-methylimidazolium chloride [BMIM]Cl at 100°C for 30 min to obtain a 7 wt% (composition ratio of cellulose: chitosan was 1:2) solution. Then, magnetic fluid was immediately added to the solution by vigorous agitation for 15 min. After several emulsion as reported in Peng et al. [131], by slowly decreasing the temperature, the composite microspheres were obtained. The final NMCMs were washed three times with deionized water followed by washing thoroughly with ethanol. Finally, the products were then stored and the yield of the microspheres production was above 95%. Results revealed that the composite microspheres exhibited efficient adsorption capacity of Cu(II) from aqueous solution, due to their favorable chelating groups in structure. Moreover, the loaded NMCMs can be easily regenerated with HCl and reused repeatedly for Cu(II) adsorption up to five cycles. Hossain et al. [32] studied the adsorption capacities of garden grass in order to remove copper (II) from water. Grass is abandoned after mowing garden, lawns and parks. In the study, the investigated garden grass was composed by three types of grasses named Kikuyu grass (*Pennisetum clandestinum*), Kangaroo grass (*Themeda australis*) and weeping grass (*Microlaena stipoides*). The foreign matters were removed from GG and washed with tap water and distilled water to remove dirt. The washed GG were kept in air for removing water from surface and dried in oven at 105°C for 24 h. The dried GG were grounded into powder and kept in air-tight bottle for using in the experiments with required amounts. Results showed that bioadsorbent from garden grass were an effective adsorbent for copper. The maximum adsorption and desorption capacity were 58.34 and 319.03 mg/g , respectively, for 1 g dose at room temperature. Furthermore, the GG had the merits of high specific surface area, significant adsorption sites and functional groups. Table 9 summarizes the main characteristics and the adsorption capacities of other sea materials-based sorbents for pollutants removal.

It is observed how the specific surface area is for 60%, 13.3%, 26.7%, 21.1% in the range of 0–10, 11–100, 101–500 m^2/g , respectively. Adsorbent dose is in the range 0.1–100 g/l. For 50% of the investigated cases, dose is 1 g/l. The specific case of 100 g/l dose corresponds to the chitosan case for 100 mg/l of initial boron concentration to be treated. Temperature varies in the range of 19.85 – 44.8°C . Only in 1 case, adsorption was conducted at temperature about 45°C . Furthermore, the available information is not always complete in line with Gautam et al. [4].

3.5. Soil and ore materials

Clays, zeolites, sediment and soil, and ore materials fall in this category. The adsorption capabilities of clay are related to the negative charge on the structure of fine grain silicate minerals. This negative charge can be neutralized by the adsorption of positively charged cations such as dyes. Besides, the clays possessed large surface area, ranging up to $800 \text{ m}^2/\text{g}$ which contributes to its high adsorption capacity [5]. There are many types of clays but montmorillonite clays are expected to have the highest sorptive capacity in comparison to other. Further, clay could be modified to enhance its efficiency for the removal of pollutants from water and wastewaters. Zeolites are naturally occurring silicate minerals, which can also be synthesized at commercial level. Probably clinoptilolite is the most abundant of >40 natural zeolite species [5]. The adsorption properties of zeolites depend upon their ion-exchange capabilities.

Sand, sediment and soil can also be utilized for the removal of organic pollutants from water. Soils have been used to remove the environmental pollutants by adsorption. Several studies reported in literature, proved their high efficiency for glyphosate [145], pesticides [146] and phenolic compounds removal [147]. Ore minerals were found suitable for the removal of organic pollutants by adsorption. As reported in Ali et al. [5], Bouyarmene et al. [148] studied natural phosphate rock and two synthetic mesoporous hydroxyapatites for the removal of pyridine and phenol from aqueous solution. Both, natural and synthetic apatites showed similar pyridine sorption capacities whereas phenol loading was proportional to their respective specific surface area. More main experiences related to the use of soil and ore materials based adsorbents are herein described.

The adsorption of methylene blue (MB) onto bentonite in a batch adsorber was studied by Ozacar and Sengil [149]. The bentonite, with a loss of ignition of 9.7, Al_2O_3 and SiO_2 content of 16.3 and 63.2% (wt%), was sieved to give different particle size fractions and the 53–75 μm particle size was used in the experiments. The BET specific surface area was measured to be $28 \text{ m}^2/\text{g}$. Furthermore, the bentonite was used directly for adsorption experiments without any treatment considering a concentration range of 100–1000 mg/l, pH 7.9 and 24.8°C . Results showed that, the design model presented by the authors is based on a pseudo second-order equation and this was used for minimizing the reaction time used in a two stage crosscurrent system. This is particularly suitable for low-cost adsorbent systems when minimizing contact time is a major operational and design criterion. The adsorption of Reactive Blue 114 (RB114), Reactive Yellow 64 (RY64) and Reactive Red 124 (RR124) by calcined alunite was studied by Ozacar and Sengil [149]. Alunite was prepared by grinding it in a laboratory type ball-mill. The alunite samples were calcined in Muffle furnace at the temperature from 100 to 800°C for 15–120 min. Then it was sieved to give 90–150, 150–250, 250–315, 315–500 and 500–710 μm size fractions. The BET surface area was 66.0 and $63.3 \text{ m}^2/\text{g}$ for 90–150 and 150–250 μm particle size range. The obtained results showed that acidic pH was favorable for the adsorption of RB114 and alkaline pH was favorable to both RY64 and RR124. Still, the adsorption capacities were found to be 170.7, 236.0 and 153.0 mg of dye per gram of calcined alunite for RB114, RY64 and RR124, respectively. The use of calcined alunite for the removal of Acid Blue 40 and Acid Yellow 17 (AB 40 and AY 17) from aqueous solution at different calcinations temperature and time, particle size, pH, agitation time and dye concentration was investigated by Ozacar and Sengil [150]. Results showed that the equilibrium saturation adsorption capacities were 212.8 mg dye/g calcined alunite and 151.5 mg dye/g calcined alunite for AB 40 and AY 17, respectively. The adsorption capacities were found to be 57.47 mg and 133.3 mg dye/g of the commercial granular activated carbon (GAC) for AB 40 and AY 17, respectively. The results indicate that, for the removal of acid dye, calcined alunite was most effective adsorbent, although comparable dye removals were exhibited by GAC. Walker et al. [151] investigated the removal of reactive dye from aqueous solution using thermally charred dolomite. The thermal processing or calcining process uses the fact that the magnesium carbonate component of the dolomite decomposes at temperatures around 800°C . This decomposition leads to changes in the chemical composition of the surface and the porosity of the mineral. The product of partial decomposition of dolomite contains calcium carbonate (calcite) and magnesium oxide showing a significant increase in specific surface area and pore volume. In this regard, the specific surface area was $36.0 \text{ m}^2/\text{g}$ correspondents to 18 h charred dolomite. Adsorption tests considering a dose of solid of 1 g/l showed that, in the initial concentration range of 100–2000 mg/l, the maximum adsorption capacity was 950.0 mg/g . Gürses et al. [152] investigated the adsorption of methylene blue onto clay. The clay sample used in the study was air dried and then sieved to give a 180–450 μm size fraction. Results showed that the adsorption capacity decreases with increasing temperature and adsorption equilibrium was attained within 1 h. It was found that clay has a mesoporous structure with an average pore

Table 9

Main characteristics and uptake capacities of various sea material sorbents for pollutants removal.

N.	Adsorbent		Adsorption test						References	
	Type	Characteristics	Pollutants to be removed	Adsorbent dose	Initial pollutant concentration range	Contact time	Temperature	pH		Amount adsorbed (q_e)
<i>Dyes removal</i>										
1	Anodonta (<i>Anodonta cygnea</i>) shell	Specific surface area = 1.42 m ² /g; particle size range of 500 and 1410 μm.	Reactive green 12	–	–	15 days	20 °C	–	0.436 mg/g	[129]
2	Anodonta (<i>Anodonta cygnea</i>) shell	Specific surface area = 1.42 m ² /g; particle size range of 500 and 1410 μm.	Direct green 26	–	–	15 days	20 °C	–	11.3 mg/g	[129]
3	Chitosan–alkali lignin composite	Specific surface area = 2.44 m ² /g	Remazol Brilliant Blue R	2 g/l	10–300 mg/l	180 min	27 °C	2.0	111.11 mg/g	[132]
4	<i>Oreochromis niloticus</i> fish scales	Specific surface area = 2.6 m ² /g	Reactive blue 5G	0.1 g/l	100–200 mg/l	1 days	30 °C	2.0	241.2 mg/g	[130]
5	Squid (<i>Loligo Tulgaris</i>) pens	Specific surface area = 8.82 m ² /g; particle size range of 500 and 1410 μm.	Reactive green 12	–	–	15 days	20 °C	–	39.8 mg/g	[129]
6	Squid (<i>Loligo Tulgaris</i>) pens	Specific surface area = 8.82 m ² /g; particle size range of 500 and 1410 μm.	Direct green 26	–	–	15 days	20 °C	–	4.83 mg/g	[129]
7	Sepia (<i>Sepia officinalis</i>) pens	Specific surface area = 4.11 m ² /g; particle size range of 500 and 1410 μm.	Reactive green 12	–	–	15 days	20 °C	–	3.46 mg/g	[129]
8	Sepia (<i>Sepia officinalis</i>) pens	Specific surface area = 4.11 m ² /g; particle size range of 500 and 1410 μm.	Direct green 26	–	–	15 days	20 °C	–	56.0 mg/g	[129]
<i>Heavy metals removal</i>										
9	Cellulose–chitosan composite	Specific surface area = 102.3 m ² /g.	Cu(II)	2 g/l	10–150 mg/l	20 h	–	5.0	65.8 mg/g	[131]
10	Chitosan	Particle size range of 100–300 μm.	Boron	100 g/l	100 mg/l	–	–	6.5	2.1 mmol/g	[133]
11	Chitosan	–	As(V)	–	0.025–2 mg/l	–	19.85 °C	5.6–6.2	0.730 mg/g	[134]
12	Chitosan	–	Cr(VI)	13 g/l	30 mg/l	–	24.85 °C	3.0	7.94 mg/g	[135]
13	<i>Cystoseira baccata</i> (Algae)	Size fraction of 0.5–1 mm	Hg(II)	2.5 g/l	–	240	25 °C	6.0	329.0 mg/g	[136]
14	Garden grass	Specific surface area = 21.28 m ² /g; particle size of 75 μm	Cu(II)	5 g/l	60–70 mg/l	7 h	20 °C	6.0–7.0	58.34 mg/g	[32]
15	<i>Gelidium sesquipedale</i> (Algae)	Particles of 0.25–1 mm size	Cd(II)	2 g/l	11.0–91.8 mg/l	60	20 °C	5.3	18.0 mg/g	[137]
16	<i>Oedogonium hatei</i> (Algae)	Specific surface area = 1.32 m ² /g	Cr(VI)	0.1–1.0 g/l	0–60 mg/l	10–160	44.8 °C	1.0–4.0	31.0 mg/g	[138]
17	Peat moss	Specific surface area > 200 m ² /g	Cd(II)	1 g/l	500 mg/l	120	–	–	5.8 mg/g	[139]
18	Peat moss	Specific surface area > 200 m ² /g	Cr(VI)	1 g/l	500 mg/l	120	–	–	29.0 mg/g	[139]
19	Peat moss	Specific surface area > 200 m ² /g	Cu(II)	1 g/l	500 mg/l	120	–	–	23.0 mg/g	[139]
20	Peat moss	Specific surface area > 200 m ² /g	Pb(II)	1 g/l	500 mg/l	120	–	–	40.0 mg/g	[139]
21	Pumice	Specific surface area = 2.34 m ² /g; chemical components: SiO ₂ (63.45%), Al ₂ O ₃ (17.24%).	Cr(VI)	6 g/l	300 mg/l	6 h	–	1	87.72 mg/g	[140]
22	Pumice modified with MgCl ₂	Specific surface area = 41.63 m ² /g.	Cr(VI)	6 g/l	300 mg/l	6 h	–	1	105.26 mg/g	[140]
23	ZVI mod. Pumice	Chemical components: SiO ₂ (66.8%), Al ₂ O ₃ (23.1%), Fe ₂ O ₃ (2.88%)	Cr(VI)	1.1 g/l	60 mg/l	60 min	25 °C	3	107.0 mg/g	[141]
24	<i>Sargassum</i> sp. (Algae)	–	Pb(II)	1 g/l	0.2–1 mM	6 h	–	5	303.0 mg/g	[142]
25	<i>Sargassum</i> sp. (Algae)	Particle of 0.3–0.7 mm size	Pb(II)	4 g/l	10–150 μg/ml	120	24.85 °C	2–7	266.0 mg/g	[143]
26	<i>Sargassum</i> sp. (Algae)	–	Pb(II)	1 g/l	0.2–1 mM	6 h	–	5	71.6 mg/g	[142]
27	<i>Ulva onoi</i> (Algae) alkali-pretreated	Pore sizes of 1 and 4 mm	Cd(II)	1 g/l	10–500 mg/l	12 h	20 °C	7.8	90.7 mg/g	[144]
28	<i>Ulva onoi</i> (Algae) untreated	Pore sizes of 1 and 4 mm	Cd(II)	1 g/l	10–500 mg/l	12 h	20 °C	7.8	61.9 mg/g	[144]

size of 34.2 nm and a BET surface area of 30 m²/g. Authors suggested that clay can be used as an effective low-cost adsorbent for the removal of cationic dyes. Eren and Acar [153] have conducted a series of batch adsorption studies for the removal of C.I. Reactive Black 5, a reactive dye, by means of a high lime fly ash. The raw fly ash was sieved to obtain various size fractions and was used without any pretreatment in the adsorption studies. Furthermore, the specific surface area was 5.35 m²/g. Results showed that the equilibrium capacity of high lime Soma fly ash was found as 7.184 mg/g dye. Based on equilibrium and kinetic results, authors suggested the use of high lime fly ash as low cost potential adsorbents for dye removal. Natural zeolite was employed as low-cost adsorbents for dye adsorption in methylene blue-containing wastewater by Wang et al. [95]. The natural zeolite contains zeolitic mineral clinoptilolite with a minor amount of mordenite, quartz, smectite, and mica. Results showed that the adsorption capacities of natural zeolite for methylene blue were 5×10^{-5} mol/g. Furthermore, investigation also indicates that adsorption is influenced by initial dye concentration, particle size, dye solution pH, and adsorption temperature. Ozdemir et al. [154] studied the adsorption mechanism of three reactive azo dyes (Reactive Black 5, Red 239 and Yellow 176) by two natural mesoporous minerals such as sepiolite and zeolite in order to identify the ability of these minerals to remove colored textile dyes from wastewaters. The adsorption results indicate that both natural sepiolite and zeolite have limited adsorption capacities of the reactive dyes but are substantially improved upon modifying their surfaces with quaternary amines. For the modification, the procedure briefly involves mixing of 5% solids with 2×10^{-2} kmol/m³ HTAB (the quaternary amines, hexadecyltrimethylammonium bromide) followed by conditioning, solid–liquid separation and drying. Hematite coated magnetic nanoparticle (MNP@hematite) was fabricated through heterogeneous nucleation technique and used to remove trace Sb(III) from water as reported in Shan et al. [155]. With saturation magnetization of 27.0 emu/g, MNP@hematite particles could be easily separated from water with a simple magnetic process in short time (5 min). At initial concentration of 110 µg/l, Sb(III) was rapidly decreased to below 5 µg/ by MNP@hematite in 10 min. Sb(III) adsorption capacity of MNP@hematite was 36.7 mg/g, which was almost twice that of commercial Fe₃O₄ nanoparticles. The removal of trace Sb(III) was not obviously affected by solution pH (over a wide range from 3 to 11), ionic strength (up to 100 mM), coexisting anions (chloride, nitrate, sulfate, carbonate, silicate, and phosphate, up to 10 mM) and natural organic matters (humic acid and alginate, up to 8 mg/l as TOC). Moreover, MNP@hematite particles were able to remove Sb(III) and As(III) simultaneously. Garcia et al. [156] investigated about the removal of arsenic (III) and arsenic (V) from an aqueous solution by means of adsorption onto Fe₃O₄, MnFe₂O₄, 50% Mn substituted Fe₃O₄, 75% Mn substituted Fe₃O₄, and Mn₃O₄ nanomaterials. From batch studies the optimum binding pH of arsenic (III) and arsenic (V) to the nanomaterials was determined to be pH 3. The binding capacity of Fe₃O₄ was determined to be 17.1 mg/g for arsenic (III) and 7.0 mg/g for arsenic (V). The substitution of 25% Mn into the Fe₃O₄ lattice showed a slight increase in the binding capacity for As(III) and As(V) to 23.8 mg/g and 7.9 mg/g, respectively. The 50% substituted showed the maximum binding capacity of 41.5 mg/g and 13.9 mg/g for arsenic (III) and arsenic (V). Furthermore, interference studies showed that SO₄²⁻, PO₄³⁻, Cl⁻, and NO₃⁻ had very minimal effects on the As(III) and As(V) binding never fell below 20% even in the presence of 1000 mg/l interfering ions.

In order to understand how polycyclic aromatic hydrocarbons (PAHs) were removed at different stages of the treatment process, adsorption experiments were conducted using quartz sand, kaolinite and natural clay as inorganic adsorbents and activated sludge as organic adsorbent for adsorbing naphthalene, phenanthrene, and pyrene [116]. Results showed that adsorption could be confirmed to be the main mechanism of PAHs removal in the WWTP. The performance of the investigated adsorbents is reported in Table 10.

It is observed how the specific surface area is for 15.8%, 76.3%, 5.3%, 2.6% e 0% in the range of 0–10, 11–100, 101–500, 501–1000 and >1000 m²/g, respectively. Adsorbent dose is in the range 0.25–50 g/l. Furthermore, dose was for the 30.8%, 23.1% and 25.6% of the cases equal to 1, 10 and >10 g/l. Temperature varies in the range of 19–30 °C highlighting how all the processes were conducted at room temperature. In addition, the available information is not always complete in line with Gautam et al. [5].

3.6. Novel low costs adsorbents

Finally, this paragraph describes some experiences of adsorbent named “novel” because they relate to the use of innovative materials such as titanium dioxide (TiO₂). In this regard, Visa and Duta [168] used fly ash to produce a novel, cost effective substrate. The new material is obtained by hydrothermal processing from fly ash coated with a wide band gap semiconductor, TiO₂. The new substrate was used removing, in a single step process, heavy metals (Cd(II) and Cu(II)) and surfactants (1-hexadecyltrimethylammonium bromide-HTAB and dodecylbenzenesulfonate-SDBS) from synthetic wastewater. The results indicated parallel adsorption of heavy metals and surfactants from wastewater and showed that, the fly ash-TiO₂ substrate, allowed efficient simultaneous removal of heavy metals and surfactants. Visa [169] investigated the possibility of using washed fly ash instead of alkali fly ash with the aim to obtain a low cost solution for advanced wastewater treatment. For improving the adsorption capacity of washed fly ash, bentonite powder was added, as a natural adsorbent with a composition almost identical to the fly ash. The new adsorbent was used on synthetic wastewaters containing methylene blue, cadmium and copper. The obtained results showed good adsorption capacity suggesting use for the pollutants removal from wastewater. In addition, Visa [169] has also considered the adsorbent disposing issue as herein discussed.

4. Outlooks and discussion

Activated carbons are the most popular and widely used adsorbents in wastewater treatment throughout the world [170]. It has several properties that make it particularly suitable for the purpose such as the high specific surface, the affinity with many compounds as well as its easy of regeneration. In spite of large use, the overall idea is to reduce the use of activated carbon because of high costs. Therefore, scientific world is looking at low-cost adsorbents as sustainable alternatives for wastewater treatment. Although numerous articles have been published in recent years, to the best of our knowledge, there are no studies which aimed to highlight the affinity of low-cost adsorbents in respect more pollutant classes. In our opinion, this is an important aspect. In fact, in order to replace the commercial activated carbon (CASs), a suitable non-conventional low-cost adsorbent should (i) be efficient to remove many and different contaminants, (ii) have high adsorption capacity and rate of adsorption and (iii) have high selectivity for different concentrations [170]. Thus, taking into account the revised literature shown in Section 3, the “adsorbents-pollutants matrices” have been drawn, systematically. For each group of adsorbents, such as agricultural and household waste, the developed matrix correlates adsorbents with pollutants. In addition, the quantification of the number of test carried out has been reported. Such a matrix, therefore, allowed answering, in a systematic way, these important questions: (1) is the adsorbent affine to more a compound? (2) If so, how many times has been tested in the literature? Furthermore, in the case of the question 1, the affinity of an adsorbent may relate the same group of pollutants such as dyes or different groups such as dyes and heavy metals.

The affinity matrices have been compiled for the five classes of pollutants investigated in Section 3. The obtained results are shown in Figs. 1, 2, 3, 4 and 5 for agriculture and household by-products,

Table 10
Main characteristics and uptake capacities of various soil and ore sorbents for pollutants removal.

N.	Adsorbent		Adsorption test							References
	Type	Characteristics	Pollutants to be removed	Adsorbent dose	Initial pollutant concentration range	Contact time	Temperature	pH	Amount adsorbed (q_e)	
<i>Dyes removal</i>										
1	Bentonite	Specific surface area = 28.0 m ² /g; 53–75 µm particle size	Basic blue 9 (Methylene blue)	1 g/l	100–1000 mg/l	180 min	24.85 °C	7.9	1667 mg/g	[149]
2	Bentonite	Specific surface area = 47.73 m ² /g	Basic red 2 (C.I. 50,240)	1.5 g/l	10 mg/l	60 min	30 °C	11.0	274 mg/g	[157]
3	Calcined alunite	Specific surface area = 66.0 m ² /g; particle size range of 90–150 µm.	Reactive yellow 64 (RY64)	10 g/l	80–100 mg/l	120 min	24.85 °C	10.0	236 mg/g	[158]
4	Calcined alunite	Specific surface area = 42.8 m ² /g	Acid blue 40 (AB40)	10 g/l	25–200 mg/l	90 min	24.85 °C	2.0	212.8 mg/g	[150]
5	Calcined alunite	Specific surface area = 42.8 m ² /g	Acid yellow 17 (AY17)	10 g/l	25–200 mg/l	90 min	24.85 °C	2.0	151.5 mg/g	[150]
6	Calcined alunite	Specific surface area = 66.0 m ² /g; particle size range of 90–150 µm.	Reactive blue 114 (RB114)	10 g/l	70–110 mg/l	120 min	24.85 °C	2.0	170.7 mg/g	[158]
7	Calcined alunite	Specific surface area = 66.0 m ² /g; particle size range of 90–150 µm.	Reactive red 124 (RR124)	10 g/l	70–110 mg/l	120 min	24.85 °C	10.0	153.0 mg/g	[158]
8	Charred dolomite	Specific surface area = 36.0 m ² /g correspondent to 18 h charred dolomite	Reactive dye Levafix Brilliant Red E-4BA	1 g/l	100–2000 mg/l	14 days	20 °C	–	950 mg/g	[151]
9	Clay	Specific surface area = 71.0 m ² /g	Basic blue 9	0.25 g/l	30 mg/l	120 min	20 °C	6.3	300 mg/g	[159]
10	Clay	Specific surface area = 30.0 m ² /g; average pore diameter (µm) = 0.0342	Basic blue 9	1 g/l	100 mg/l	120 min	19.85 °C	–	6.3 mg/g	[152]
11	Diatomite	Specific surface area = 33.0 m ² /g; particle size range of 45–63 µm;	Basic blue 9	0.8 g/l	0.13–1.87 mmol/l	3 days	25 °C	7.0	0.42 mmol/g	[160]
12	Diatomite	Specific surface area = 27.8 m ² /g; particle size range of 106–250 µm.	Basic blue 9	0.83 g/l	100–400 mg/l	2 days	20 °C	10.0–11.0	198 mg/g	[161]
13	DTMA-bentonite (Dodecyltrimethylammonium bromide-modified bentonite)	Specific surface area = 767.0 m ² /g	Acid blue 193	2 g/l	–	60 min	20 °C	–	740.5 mg/g	[162]
14	High lime fly ash	Specific surface area = 5.35 m ² /g	Reactive black 5	2.5–15.0 g/l	100 mg/l	60 min	20 °C	5.0–6.0	7.184 mg/g	[153]
15	Modified sepiolite	Specific surface area = 50.5 m ² /g; SiO ₂ = 52.76%; MgO = 15.17%; loss of ignition = 21.42%.	Reactive black 5	50 g/l	25 g/m ³	120 min	22.5 °C	–	120.5 mg/g	[154]
16	Modified sepiolite	Specific surface area = 50.5 m ² /g; SiO ₂ = 52.76%; MgO = 15.17%; loss of ignition = 21.42%.	Reactive red 239	50 g/l	25 g/m ³	120 min	22.5 °C	–	108.8 mg/g	[154]
17	Modified sepiolite	Specific surface area = 50.5 m ² /g; SiO ₂ = 52.76%; MgO = 15.17%; Loss of Ignition = 21.42%.	Reactive yellow 176	50 g/l	25 g/m ³	120 min	22.5 °C	–	169.1 mg/g	[154]

(continued on next page)

Table 10 (continued)

N.	Adsorbent		Adsorption test						References	
	Type	Characteristics	Pollutants to be removed	Adsorbent dose	Initial pollutant concentration range	Contact time	Temperature	pH		Amount adsorbed (q_e)
18	Modified silica	Specific surface area = 269.0 m ² /g; Particle size range of 30–75 µm.	Acid blue 25 (C.I. N. 62,055)	2 g/l	–	–	20 °C	–	45.8 mg/g	[163]
19	Modified zeolite	Specific surface area = 11.8 m ² /g	Reactive black 5	50 g/l	25 g/m ³	120 min	22.5 °C	–	60.5 mg/g	[154]
20	Modified zeolite	Specific surface area = 11.8 m ² /g	Reactive red 239	50 g/l	25 g/m ³	120 min	22.5 °C	–	111.1 mg/g	[154]
21	Modified zeolite	Specific surface area = 11.8 m ² /g	Reactive yellow 176	50 g/l	25 g/m ³	120 min	22.5 °C	–	88.5 mg/g	[154]
22	Zeolite	Specific surface area = 16.0 m ² /g; Loss of ignition = 12.5%.	Basic blue 9	0.5 g/l	1.9 × 10 ⁻⁵ M	100 h	–	9.0	0.045 mmol/g	[95]
<i>Heavy metals removal</i>										
23	Bentonite	Specific surface area = 99.0 m ² /g	Sb(III)	25 g/l	0.05–4 mg/l	24 h	24.85 °C	6.0	0.500 mg/g	[164]
24	Bentonite	Specific surface area = 99.0 m ² /g	Sb(V)	25 g/l	0.05–4 mg/l	24 h	24.85 °C	6.0	0.556 mg/g	[164]
25	Diatomite	The mineralogical composition of the dried sample supplied by the company is 92.8% SiO ₂ , 4.2% Al ₂ O ₃ , 0.3% MgO, 1.5% Fe ₂ O ₃ , 0.6% CaO, and 0.5% other oxides.	Sb(III)	–	10–400 mg/l	–	19.85 °C	6.0	35.2 mg/g	[165]
26	HDTMA-modified natural mordenite (SMNM)	Specific surface area = 8.9 m ² /g	As(V)	10 g/l	5–250 mg/dm ³	–	22.85 °C	6.0	97.3 mg/g	[166]
27	Goethite	Specific surface area = 106.0 m ² /g	Sb(V)	25 g/l	0.05–15 mg/l	24 h	24.85 °C	7.0	18.3 mg/g	[167]
28	HDTMA(cationic surfactant hexadecyltrimethylammonium-bromide)-clinoptilolite (SMNC)	Specific surface area = 7.3 m ² /g	As(V)	10 g/l	5–250 mg/l	–	22.85 °C	6.0	45.3 mg/g	[166]
29	Hematite coated magnetic nanoparticle (MNP@hematite)	MNP@hematite particles were spherical in shape with size of 10–30 nm. The composite material was superparamagnetic, with a saturation magnetization of 27.0 emu/g.	Sb(III)	80.5 g/l	1–20 mg/l	–	24.85 °C	4.1	36.7 mg/g	[155]
30	Mixed ferrite and hausmannite nanomaterials	Particle size range of 15–20 nm	As(III)	10 g/l	3–1000 mg/l	–	–	3.0	41.5 mg/g	[156]
31	Zeolite (natural clinoptilolite, NC)	Specific surface area = 21.9 m ² /g	As(V)	10 g/l	5–250 mg/l	–	22.85 °C	6.0	9.33 mg/g	[166]
32	Zeolite (natural mordenite, NM)	Specific surface area = 20.1 m ² /g	As(V)	10 g/l	5–250 mg/l	–	22.85 °C	6.0	17.3 mg/g	[166]
<i>Other pollutants removal</i>										
33	Clay	Specific surface area = 18.75 m ² /g	Naphthalene (NAPT)	1 g/l	500–600 µg/l	24 h	25 °C	–	45 µg/g	[116]
34	Clay	Specific surface area = 18.75 m ² /g	Phenanthrene (PHEN)	1 g/l	900–1000 µg/l	24 h	25 °C	–	55 µg/g	[116]
35	Clay	Specific surface area = 18.75 m ² /g	Pyrene (PYR)	1 g/l	300–400 µg/l	24 h	25 °C	–	360 µg/g	[116]
36	Kaolin	Specific surface area = 15.63 m ² /g	Naphthalene (NAPT)	1 g/l	600–800 µg/l	24 h	25 °C	–	44 µg/g	[116]
37	Kaolin	Specific surface area = 15.63 m ² /g	Phenanthrene (PHEN)	1 g/l	600–800 µg/l	24 h	25 °C	–	50 µg/g	[116]
38	Kaolin	Specific surface area = 15.63 m ² /g	Pyrene (PYR)	1 g/l	200–300 µg/l	24 h	25 °C	–	270 µg/g	[116]
39	Quartz sand	Specific surface area = 6.38 m ² /g	Naphthalene (NAPT)	1 g/l	600–800 µg/l	24 h	25 °C	–	40 µg/g	[116]
40	Quartz sand	Specific surface area = 6.38 m ² /g	Phenanthrene (PHEN)	1 g/l	600–800 µg/l	24 h	25 °C	–	45 µg/g	[116]
41	Quartz sand	Specific surface area = 6.38 m ² /g	Pyrene (PYR)	1 g/l	300–400 µg/l	24 h	25 °C	–	200 µg/g	[116]

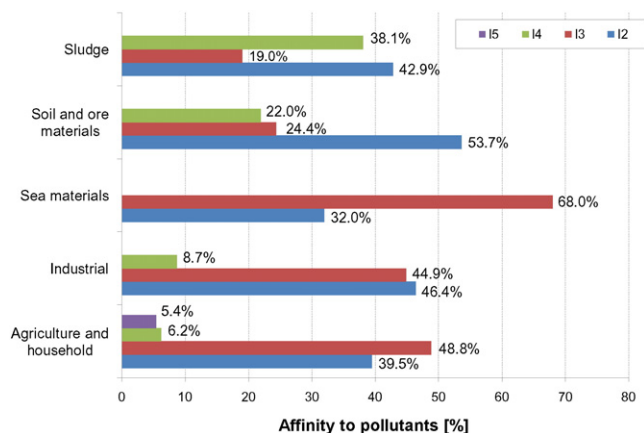


Fig. 6. Affinity of low-cost adsorbents to pollutants. In the figure: I_1 = total number of low-cost adsorbent for each category (agriculture and household; industrial; sea materials; soil and ore materials; sludge); I_2 = Affinity to dyes evaluated as the percentage of the ratio “number of adsorbents affine to dyes”/ I_1 ; I_3 = Affinity to heavy metals evaluated as the percentage of the ratio “number of adsorbents affine to heavy metals”/ I_1 ; I_4 = Affinity to biorecalcitrant compounds evaluated as the percentage of the ratio “number of adsorbents affine to biorecalcitrant compounds”/ I_1 ; I_5 = Affinity to phosphate and nitrogen compounds evaluated as the percentage of the ratio “number of adsorbents affine to phosphate and nitrogen compounds”/ I_1 .

industry such as automotive was considered. With the aim to remove the hexavalent chromium, commercial activated carbon and the calcinated cereal by-product were tested [174]. The obtained results showed that the performance of the novel product, derived from agriculture wastes, was comparable to commercial AC.

The possibility to use traditional inorganic adsorbents and activated sludge in combined way was also investigated by Liu et al. [116]. According to them, inorganic particles such as quartz sand, kaolinite, and natural clay allowed the adsorption of naphthalene, phenanthrene, and pyrene (the most commonly PAHs) in the primary settling tank while the organic one, such as activated sludge derived sorbents, the removal of the same compounds directly in the oxidation basin. Fig. 7 illustrates how those above mentioned processes can be integrated in sequence for biorecalcitrant compounds removal. Furthermore, Fig. 7 shows an important technological aspect. In order to scale-up the treatment scheme presented by Liu et al. [116], it is important that the wastewater treatment plant is equipped (at least) with filtration phase based, for example, on the use of sand. In fact, filtration separates the adsorbents added in the biological phase in such a way that suspended solids comply with the target sets imposed by law. In this regard, full-scale experiences conducted by EAWAG (Swiss Federal

Institute of Aquatic Science and Technology) at the Kloten-Opfikon wastewater treatment plant in Zurich, Switzerland (60.000 population equivalent), show how the secondary sedimentation (See also Fig. 7) properly allowed the solid/liquid separation with values of the Sludge Volume Index (SVI) in line with the characteristics of a good sludge sedimentability (150–200 ml/g). However, the main problem was the increase of the filter backwash solids mass flow-rate Grassi [176]. Practically, the problem was moved from the water to the sludge line of the plant and few investigations have been carried out on sludge.

Additional discussion points concern (i) the regeneration of adsorbent and (ii) the possibility of increasing their life avoiding the use of the commercial activated carbon available on the market.

For the first point, it is well known of the main disadvantage connected to the implementation of adsorption processes is linked to the cost of regeneration of the adsorbent material employed, especially if it is realized by means of a thermal process, due to the consumption of energy and to the transport off-site. Among the handful, Tolba et al. [177] investigated the adsorption capacity of nanosilica derived from the rice husk for the removal of methylene blue. The results indicated that silica can be recycled by a simple heat treatment retaining the high removal efficiency in four successive cycles and suggesting their potential application in water treatment. They showed how 99.6% of methylene blue were removed in 40 min in the third cycle for the initial concentration 10 mg/l as well as increased for the other initial concentrations. Ghasemi et al. [178], considering two new adsorbents, ash and Fe nanoparticles loaded ash (nFe-A) for the removal of Pb(II) from aqueous solution, highlighted how the regeneration studies carried out showed promising regeneration potential of these adsorbents. The breakthrough capacities of ash and nFe-A for Pb(II) removal was found 25 and 30 mg/l, respectively.

For the second point, Visa [169] highlights the possibility of using the adsorbent at the end of their life for further purposes avoiding landfill disposal. Considering the simultaneous removal of heavy metals and methylene blue from wastewater resulted in the dyes finishing industry, they showed how, using washed fly ash and bentonite as substrate, the pollutants can be removed at low cost by adsorption. Further, the spent adsorbent annealed at 500 °C was included in stone blocks resulting hybrid inorganic–organic composites. Thus, the obtained results suggested the reuse of spent adsorbent for padding in the stone blocks.

Finally, it is interesting to point out how cost of commercial adsorbents is still high. Although costs should be considered indicative because of adsorbent costs depend on many factors (availability, its source such as natural, industrial/agricultural/domestic waste or by-products or synthesized products, treatment conditions, recycle and lifetime issues, country of production such as developed, developing or underdeveloped), the cost of commercial activated carbon (for

Table 11

Several case studies concerning low-costs adsorbents versus commercial activated carbons for wastewater treatment.

N.	Type of wastewater	Pollutant to be removed	Where adsorption take places?	Adsorbent		Performance		Reference
				Novel	Commercial	Novel	Commercial	
1	Industrial (Textile effluent) ^a	Safranin-T (dye)	Coagulation, flocculation, reverse osmosis and adsorption.	Activated rice husks (ARH)	Activated carbon (AC)	0.014 mol/g (q_e)	0.526 mol/g (q_e)	Gupta et al., [173]
2	Industrial ^b	Fluoride	Adsorption column	Carbon slurry (CS)	Activated carbon (AC)	4.86 mg/g (q_e)	1.10 mg/g (q_e)	Gupta et al., [175]
3	Industrial (Textile effluent) ^c	Direct Blue 85 (dye)	Oxidation unit (SBR)	Metal hydroxide sludge (WS)	Activated carbon (AC)	339 mg/g (q_e)	7.69–18.7 mg/g (q_e)	Santos and Boaventura [171]
4	Industrial (Surface treating industry, i.e., automotive, medical) ^d	Chromium (VI)	Adsorption column	Calcinated cereal by-product (CBP)	Activated carbon (AC)	90.37% (percentage removal)	89.85% (percentage removal)	Arris et al. [174]

^a Dye concentration = 5.0×10^{-5} M; pH 6.5; amount of AC = 0.10 g and amount of ARH = 0.05 g; sieve size = 0.3–0.15 mm (for each); $1/C_e = 40$ l/mol; Temperature = 60 °C; $1/q_e$ for AC-system = 1.9 g/mol; $1/q_e$ for ARH-system = 72 g/mol [173].

^b Initial fluoride concentration = 15.0 mg/l; Adsorbent dose = 1.0 g/l; pH = 11 [175].

^c Dye concentration = 85 mg/l; Adsorbent dosage = 1 g/l; pH = 7; Temperature = 25 °C; $C_e = 100$ mg/l [171].

^d pH range of 6–8 for an initial chromium concentration of 132 mg/l [174].

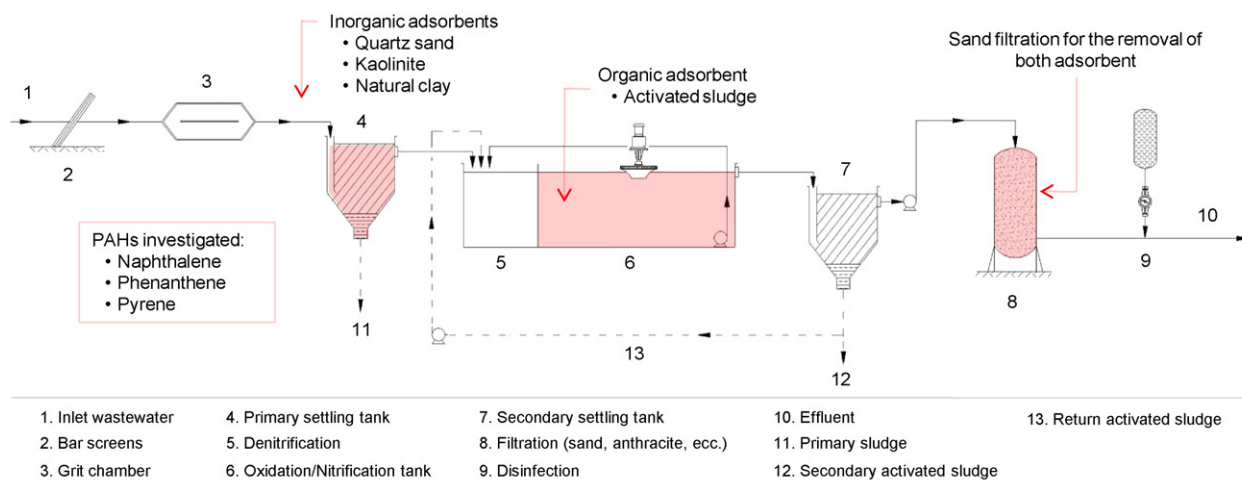


Fig. 7. Combination of inorganic adsorbents and activated sludge (as organic adsorbent) for the removal of PAHs from a municipal wastewater treatment plant.

example, the Filtrasorb 400) was on average higher than 90% compared to that of novel adsorbents such as bagasse fly ash, red mud or blast furnace slag [170]. In particular, Table 12 compares several costs considering two recent references [8,170].

Çifçi and Meriç [8] highlight how chitin and chitosan showed prices very high compared to other adsorbents. Additionally, Filtrasorb 400, available on market, showed little variable costs over time (2012–2015). According to Çifçi and Meriç [8], among the adsorbents used, the price of pumice is the lowest (about 100 times cheaper than that of chitin, chitosan, and activated carbon). Grassi et al. [170] shows how industrial by-products such as bagasse fly ash, blast furnace slag, peat and red mud are among the most competitive.

5. Concluding notes

Based on the extensive literature reviewed, the following outcomes can be drawn:

- There is a lack of data concerning the characteristics of the investigated novel by-products. In many cases, adsorption tests were conducted without highlighting the characteristics of the adsorbents such as their average particle size or specific surface area. Furthermore, with

Table 12
Cost evaluation of different adsorbents.

Adsorbents	Commercial prize [US\$/kg]	
	Grassi et al. [170]	Çifçi and Meriç [8]
Activated alumina	–	1.5–3.5
Bentonite	–	0.05–0.2
Activated charcoal	–	1.0–1.1
Bagasse fly ash	0.02	–
Blast furnace slag	0.04	–
Carbonaceous adsorbent from fertilizer industry waste	0.1	–
Clinoptilolite	–	0.14–0.29
Chitin	–	15–20
Chitosan	16	5–10
Cross-linked-chitosan	–	5–10
Coconut shell charcoal	0.34	0.5–0.8
Natural zeolite	0.08	–
Non-cross-linked chitosan	–	5–10
Peat	0.04	–
Pumice	–	0.12–0.3
MgCl ₂ pumice	–	0.12–0.3
ZVI mod. Pumice	–	0.12–0.3
Red mud	0.025	–
Commercial activated carbon (CAC) ^a	–	0.8–1.1
Activated Carbon (Filtrasorb 400) ^a	21	20–22

^a State-of-the-art.

reference to adsorption tests in batch mode, it was not always possible to acquire information on important parameters such as adsorption dose, contact time and initial pollutant concentration. Consequently, there is still much study to be done in order to standardize the outputs of each research.

- Since there is a little knowledge about the comparison studies of sorbents for pollutants removal, we think that the elaboration of simple methodological tools such as the “adsorbents-pollutants” matrices could give useful information in identifying those adsorbents with a greater affinity towards more pollutants. Considering agriculture and household by-products, banana and orange peels showed a greater affinity for the removal of dyes, heavy metals and other pollutants such as phosphorous and nitrogen compounds. Instead, among industrial ones, the best in this direction are the furnace slag, carbonaceous adsorbents from fertilizer industry, fly ash and red mud. Still, among some industrial by-products, fly ash could be used in combination with other technologies (we think stabilization/solidification treatments) in order to replace the commercial activated carbon correctly used;
- According to the literature reviewed, novel low-costs adsorbents represent a promising green technology. Potentially, they can be applied at full-scale wastewater treatment. However, most of studies published in literature were referred to experimentations at lab-scale. Furthermore, the majority of the studies focused on synthetic solutions with only few studies using real wastewater.
- Ultimately, in order to take into account the new frontiers of research, the regeneration of the novel adsorbents as well as the study of their end of life should be carefully evaluated.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.susmat.2016.06.002>.

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