Typical low cost biosorbents for adsorptive removal of specific organic pollutants from water

Van Son Tran[a], Huu Hao Ngo[a*], Wenshan Guo[a] , Jian Zhang[b], Shuang Liang[b], Cuong Ton- That[c], Xinbo Zhang[d]

[a]Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology Sydney, Broadway, NSW 2007
[b] Shandong Provincial Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Jinan 250100, China
[c]School of Physics and Advanced Materials, University of Technology Sydney, Broadway, NSW 2007
[d]School of Environmental and Municipal Engineering, Tianjin Chengjian University, Tianjin 300384, China

* Correspondence author. Tel: +61 2 9514 2745; Fax: + 61 2 9514 2633.
Email address: h.ngo@uts.edu.au

Abstract

Specific organic pollutants (SOPs) such as phenolic compounds, PAHs, organic pesticides, and organic herbicides cause health and environmental problems due to their excessive toxic properties and poor biodegradability. Low-cost biosorbents are considered as a promising alternative for conventional adsorbents to remove SOPs from water. These materials have several advantages such as high sorption capacities, good modifiability and recoverability, insensitivity to toxic substances, simple operation in the treatment processes. However, previous reports on various types of biosorbents for removing SOPs are still moderately fragmented. Hence, this paper provides a comprehensive review on using typical low-cost biosorbents obtained from lignocellulose and chitin/chitosan for SOPs adsorption. Especially, their characteristics, biosorption mechanism together with utilization for eliminating SOPs are presented and discussed. The paper also gives a critical view regarding future applications of low-cost biosorbents in SOPs-contaminated water treatment.

Key words: Low-cost biosorbents, specific organic pollutants (SOPs), adsorption mechanism, removal capacity, water

1. Introduction

Organic pollutants have become an increasing concern due to their potential of mutagenicity, carcinogenicity, teratogenicity and high bioaccumulation (Abdeen and Mohammad, 2013; Chen et al., 2011; Valili et al., 2013; Masiá et al., 2014; Julian et al., 2013). The adverse effects on health and the environment caused by specific organic pollutants (SOPs) such as phenolic compounds, polycyclic aromatic hydrocarbons (PAHs) and agricultural chemicals (organic pesticides and organic herbicides) have been considered as critical problems (Chen et al., 2011; Ahmed and Mohammad, 2014; Nanseu-Njiki et al., 2010; Nagda et al., 2007). World Health Organization has established a very strict legislation for these compounds in WHO (2011) Guideline for Drinking-Water Quality (Fourth Edition). For example, the limits of 2,4,6 trichlorophenols (phenolic compound), Benzo(a)pyrene (PAH), Dichlorodiphenyltrichloroethane and metabolites (pesticide), and 2,4-Dichlorophenoxyacetic acid (herbicide) were set at 200×10^{-3}, 0.7×10^{-3}, 1×10^{-3}, and 30×10^{-3} mg/L, respectively. As a consequence, abatement of these compounds from water is indispensable for protecting human health and the environment.

Several available techniques (e.g. photocatalytic degradation, combined photo-fenton and ultrasound, advanced oxidation, aerobic degradation, filtration, ozonation, coagulation, flocculation, distillation, extraction, precipitation, and adsorption, etc.) have been developed for SOPs removal from water (Ahmad et al., 2010; Ahmed and Mohammad, 2014; Al-Zaben and Mekhamer, 2013; Kong et al., 2012; Pal, 2012; Pham et al., 2012). Among them, adsorption has superior advantages over other methods for removing pollutants at low concentration with respect to environmental friendliness, economy and high efficiency (Chen et al., 2011; Xi and Chen, 2014; Yakout and Daifullah, 2013). Nevertheless, the expensive manufacturing cost makes conventional adsorbents such as activated carbon less economically feasible for extensive use in water treatment (Ata et al., 2012). The use of non-conventional, low-cost biosorbents prepared from agricultural wastes and by-products can not only reduce a large quantity of solid waste but also be very attractive. Their benefits are mentioned, including low investment cost, simplicity of design and operation, insensitivity to toxicants and a remarkable performance even with very low concentration solutions (Mohammad, 2013). It was reported that biosorption could reduce 20, 36 and 28 % of capital, operational and total cost in comparison with conventional systems, respectively (Ata et al., 2012).

The uptake capacity and stability of biomaterials can be enhanced by physical and chemical modifications with heat (drying and pyrolysis), de-sugared, and inorganic/organic activants (e.g. H_3PO_4, HNO_3, HCl, H_2SO_4, NaOH, $KMnO_4$, CH_3OH, methacrylic, methanol, acetone, etc.) (Abdeen and Mohammad, 2013; Akhtar et al., 2006; Li et al., 2009; Nagda et al., 2007; Xi and Chen, 2014; Yakout and Daifullah, 2013). In addition, tons of cheap biosorbents belonging to some principal categories (including lignocellulose, algae, chitin/chitosan, activated sludge, bacteria biomass, fungal biomass, and so on) are able to be used for SOPs removal (Aksu, 2005; Abdolali et al., 2014, Ahmad et al., 2010). Among these categories, lignocellulose and chitin/chitosan are great applicable groups because of their representativeness, high adsorption capacity and availability. In terms of sorption capacity, it is determined by either the presence of lignin and silica in lignocellulose structure, or the rich contents of amino and hydroxyl functional groups in chitosan or chitin's derivative (Xi and Chen, 2013, Abdeen and Mohammad, 2014).

Although applications of biosorbents on treating heavy metals have been extensively examined (Abdolali et al., 2014; Nguyen et al., 2013; Hossain et al., 2012), studies on removing SOPs were only emerging in recent years (Ahmad et al., 2010; Bhatnagar and Sillanpää, 2009; Srivastava et al., 2009; Zolgharnein et al., 2011). Research on this issue mostly focused on single groups of SOPs on different types of adsorbents. For instance, papers on pesticide removal from water by different materials including conventional and low-cost biosorbents mainly focused on adsorption capacities as well as experimental conditions (Ahmad et al., 2010; Srivastava et al., 2009; Zolgharnein et al., 2011). There is a lack of reviews discussing relationship between characterization of biosorbents and mechanism as well as adsorption capacities for all four kinds of SOPs (Phenols, PAHs, pesticides and herbicides).

To demonstrate the feasibility of using low-cost biosorbents prepared from lignocellulose and chitin/chitosan for SOPs removal, this paper presents a comprehensive review with focused discussions on five key sections: (i) characteristics, (ii) biosorption mechanisms, (iii) maximum adsorption capacities, (iv) methods to produce better biosorbents and (v) utilization of biosorbents for SOPs removal.

2. Characteristics of typical biosorbents

Physical and chemical characteristics of biosorbents are very important to understand adsorption mechanism as well as potential application of the materials. Therefore, this section discusses the characterization of typical low-cost materials from lignocellulose and chitin/chitosan. Table 1 summarizes the characteristics of biosorbents which determined their adsorption process for SOPs from water.

Table 1

2.1. Lignocellulose

Key characteristics for determining SOPs adsorption on lignocellulosic materials include chemical composition, functional groups, surface area, porosity and surface morphology.

The most significant characteristic of lignocellulose affecting its adsorption behavior is chemical composition. As the primary building block of plant cell walls, lignocellulose contains cellulose, hemicellulose, lignin and a little amount of pectin, protein, vitamins, lipids, extractives, combined with ash (Jørgensen et al., 2007). Chemical compositions of lignocellulose can be characterized by X-ray Photoelectron Spectroscopy, X-ray Diffraction, and chemical analysis. The chemical compositions of some typical low-cost lignocellulosic adsorbents are shown in Fig. 1 (Ferraz et al., 2000; Ismail et al., 2002; Khalil et al., 2007; Khiari et al., 2010; Krishnani et al., 2008). Plants residues such as wooden materials, coconut shell, pineapple leaves, banana stem, sugar cane bagasse, coffee waste have the highest cellulose contents (>40%). The highest lignin content (>30%) appears in biomass like neptune grass, soft wood, coconut shell and bark. According to Xi and Chen (2014), adsorption capacities of biosorbents could be affected by some factors such as polarity and aromaticity. In which lignin is assumed to be the main storage medium of organic pollutants and higher lignin content results in higher affinity with persistent organic pollutants. The authors further pointed out that the adsorption potential of lignin was seriously restricted by polar components. This hypothesis suggested that low sugar content (polar component) could enhance adsorption ability of pine needles for persistent organic pollutants (Chen et al., 2011). In addition, ash content of lignocellulose also played an important role in the adsorption process of organic pollutants on these materials. The ionic structure of silica

($SiO_4 \cdot 4H_2O$) in ash content provides a capability of adsorbing polar molecules as phenols (Akhtar et al., 2006).

Fig. 1.

Another important factor for binding SOPs on lignocellulose is the existence of functional groups such as hydroxyl (-OH), carboxyl (-COOH) and silanol (Si-OH), which are responsible for sorption of organic pollutants from the aquatic environment (Akhtar et al., 2006; Aksu, 2005; Krishnani et al., 2008; Abdolali et al., 2014). According to Mohammad (2013), functional groups are responsible for pesticides removal by lignocellulosic materials. Olivella et al. (2013) also proposed mechanisms of phenanthrene sorption by cork relating to aromatic rings of lignin and carboxyl groups ($-COO^-$) in the biosorbent. Functional groups of lignocellulosic materials were often qualitatively determined by Fourier Transform Infrared Spectroscopy (FTIR). Xi and Chen (2014) employed FTIR technique to explore sorption mechanism of PAHs on several raw and modified plant residues and found that aromatic bands were major functional groups in de-sugared materials which has better adsorption capacities than raw biomass. The authors concluded that the de-sugared or hydrolyzed biomasses are promising biosorbents for removing PAHs. From FTIR analysis, Ahmed and Mohammad (2014) reported that some surface functional groups such as -OH, alkyne, aromatic rings, ketone, aldehydes, lactones and carboxyl might be involved in the pesticide removal on apricot stone activated carbon.

The surface area and porosity of lignocellulose that were analyzed by Brunauer–Emmett–Teller (BET) method also greatly affect their SOPs adsorption capacities. The International Union of Pure and Applied Chemistry (IUPAC) recommended classification of materials based on their total porosity. Accordingly, adsorbents can be divided into three categories, namely macropores (d>50 nm), mesopores (2<d<50 nm) and micropores (d<2 nm). In raw form, the surface areas of plant residues are quite small, for example, surface area of some biomass including wood chips, ryegrass roots, orange peel, bamboo leaves, pine needles were in a range of 3.41 - 25.97 m^2/g (Chen et al., 2011). On the contrary, after modification, surface area and porosity of lignocellulose can be increased, the surface area and porosity of apricot stone activated carbon were 566 m^2/g and 0.32 nm, respectively (Mohammad, 2013). Ioannidou et al. (2010) stated that the surface area and porosity of lignocellulose were affected by ash content. The authors demonstrated that biomasses with higher ash content tend to create activated carbons with higher mesopore volumes than the ones with lower ash content. These biosorbents have lower surface area and then lower adsorption capacities for organic compounds.

The last principal factor of lignocellulose which decides sorption capacity is surface morphology (topographical and elemental information) (Kong et al., 2012). Scanning Electron Microscope (SEM) is the method was often utilized to determine this characterization. Based on SEM results, Islam et al. (2009) indicated that pores and opening structures on the surface of used tea leaves mainly responsible for quinalphos adsorption.

The above nature of lignocellulose provides them ability to adsorb SOPs. Furthermore, adsorption capacity of organic pollutants on biosorbents can be enhanced by modifications of raw materials with various methods. A treatment of raw lignocellulose that will remove part of organic matter such as carbohydrates (cellulose), and increase its surface area and porosity is needed before using it for organic pollutant removal (Valili et al., 2013). Chemicals like NaOH, methanol, hydrogen chloride, CH_3OH, HCl are not effective whilst thermal treatment under oxygen-limited conditions produce significantly better biosorbents for such pollutants. Valili et al. (2013) reported that pyrolysis is a good method for producing better biosorbents due to the dependence of organic pollutants adsorption on the total organic carbon content and the porosity of the materials (Valili et al., 2013). The authors demonstrated that thermal treated biosorbents are more favorable for eliminating organic pollutants than sorbent produced from coal.

2.2. Chitin/chitosan

Chitin, a naturally mucopolysaccharide, is created by a vast number of living creatures such as in the exoskeletons of crabs, other arthropods and cell walls of some fungi, and was seen as the most natural polymer after cellulose in terms of abundant (Bailey et al., 1999; Ravi Kumar, 2000). The production of this biopolymer is associated with seafood processing such as shrimp or crab canning. A crucial derivative of chitin is its deacetylated form namely chitosan or glucosamine that can be chemically prepared from chitin. In comparison with lignocellulose, characteristics of chitin/chitosan which determine SOPs adsorption process on the materials are molecular chemical structure, functional groups and surface area.

The first vital characteristic of chitin/chitosan is their molecular chemical structure. The compounds are highly hydrophobic and insoluble in water as well as most organic solvents (Ravi Kumar, 2000). Chitin consists of 2-acetamido-2-deoxy-β-D-glucose through a β (1 - 4) linkage and can be degraded by chitinase (Ravi Kumar, 2000). Chitosan is made from D-glucosamine and N-acetyl-D-glucosamine units while the protonation of amine groups provides its affinity for anionic contaminants such as metal anions, organic compounds, dyes.

Functional groups play another principal role in SOPs adsorption of chitin/chitosan. Abdeen and Mohammad (2013) employed FTID to analyze functional groups of chitosan. The results showed that chitosan has some functional groups such as hydroxyl

(-OH), amino (-NH_3^+), methyl carboxyl (- CH_2COOH), (C=O) of acetyl, amide (-$CONH_2$) that are involved in the removal of ethoprophos. The high contents of amino and hydroxyl functional groups in chitosan make it become a high potential material for removing various types of aquatic pollutants (Bhatnagar and Sillanpää, 2009).

The last significant feature to SOPs adsorption of chitin/chitosan is their surface area. Surface area of chitin/chitosan is much less than lignocellulose. For example, from BET analysis, Li et al. (2008) reported that surface area of pure chitosan beads, chitosan-TiO_2 beads were 0.654 and 1.342 m^2/g, correspondingly. Comparison between flakes chitosan and highly swollen beads chitosan indicated that uptake capacity of pentachlorophenol depends on specific surface area of the materials (Bhatnagar and Sillanpää, 2009).

Natural chitosan has been modified by a number of techniques to improve SOPs adsorption capacity as well as application potential in water treatment. Different kinds and shapes of chitosan such as magnetite-immobilized chitin, beads of chitosan-sodium alginate, functional chitosan, membranes, microspheres, gel beads and films were prepared and examined for eliminating various contaminants from the aquatic environment (Bhatnagar and Sillanpää, 2009). After modification, surface area and morphology of chitosan has become much more favourable for SOPs abatement. For example, characterization of beads of chitosan-sodium alginate are surface area of 102.15 m^2/g, pore volume of 0.5 cm^3/g, porosity of 52.36%, pore diameter of 0.87 nm, and density of 2.15 g/cm^3, and includes functional groups such as -OH, -NH_2, and -COOH (Nadavala et al., 2009).

3. Mechanism of SOPs adsorption on biosorbents

An insight into adsorption mechanisms of SOPs on biosorbents support evaluation of application potential coupled with the development of methods to produce better materials. Adsorption mechanisms depend on characteristics of biosorbents and nature of adsorbates. There are some interactions relating to the mechanism of SOPs removal from water by biosorbents such as Van der Waals, dipole-dipole interactions, electrostatic forces, and weak intermolecular associations (Pal, 2012). Adsorption mechanism of organic toxicants on biosorbents is still a controversial issue that no simple theory can adequately explain adsorption characteristics (Nalcaci et al., 2011). Thus, FTIR, SEM, adsorption energy model (Dubinin-Radushkevich), pH, etc. are crucial. Presently, several mechanisms proposed in adsorption of SOPs by biosorbents include partition, diffusion, cation exchange, hydrogen bond, electrostatic interaction and so forth.

Partition process was often assumed is the main mechanism for removal of SOPs by biosorbents. In their study, Chen et al. (2011) examined PAHs removal by plant residue such as wood chip, ryegrass root, orange peels, bamboo leaves, and pine needles. The practically linear isotherms results showed that partition process is the predominant mechanism for the plant residues biosorbents. The authors used partition coefficient (Kd) to estimate sorption capacity of sorbents. The Kd values increased in the order of wood chip (2484±24.24 L/kg) < ryegrass roots (2777±58.62 L/kg) < orange peels (2970±39.80 L/kg) < bamboo leaves (3746±96.54 L/kg) < pine needles (5306±92.49 L/kg). More recently, the same results were obtained by Xi and Chen (2014) in using raw and modified biosorbents for removing PAHs. The sorption isotherms indicated a predominant partition process and Kd values of the four raw plant residues for phenanthrene ranked in the order of bamboo wood (2896 L/kg) < pine bark

(5445 L/kg) < pine needles (6370 L/kg) < pine wood (6754 L/kg). The research specified negative role of polysaccharides and sugar contents in adsorption capacity of pollutants on biosorbents. The Kd values of phenanthrene onto the four modified plant residues ranked in the order of pine bark-desugared (32693 L/kg) < pine needles-desugared (38375 L/kg) < bamboo wood-desugared (51464 L/kg) < pinewood-desugared (55763 L/kg). Li et al. (2010) also pointed out that adsorption capacity of aromatic domains on pine wood and pine needles was utterly decreased with high polysaccharide component. As a result, acid hydrolysis was a useful technique to improve adsorption properties of biosorbents. The research results stated that the adsorption processes were controlled by a partition mechanism. The partition coefficients (Kd) by pine wood and pine wood-desugared were 270 and 2124 L/kg for naphthalene, 1365 and 10804 L/kg for acenaphthene, 6754 and 55763 L/kg for phenanthrene, 26833 and 218233 L/kg for pyrene, respectively.

In a research on carbofuran and methyl parathion biosorption onto chestnut shells, the adsorption rate was chiefly directed by intraparticle diffusion and to less extent by film diffusion (Zolgharnein et al., 2011). The mechanism of an adsorption process can be predicted by Dubinin-Radushkevich model, in which adsorption energy will be calculated as this equation: $E = 1/\sqrt{2\beta}$, where β (mol^2/J^2) is an experimental constant (Abdeen and mohamamd, 2014). If the adsorption energy value range from 8 to 16 kJ/mol, the process is dominated by ion exchange mechanism while if the value is less than 8 kJ/mol, the adsorption process is controlled by physio-sorption.

Cation exchange was the proposed mechanism by Nanseu-Njiki et al. (2010) for paraquat removal by Ayous sawdust. The experimental results of adsorption energy determined from the Dubinin-Radushkevich model (12.0247 kJ/mol) suggested the involvement of the cation exchange mechanism during adsorption. Intra-particle diffusion model indicated that biosorption rate of paraquat on sawdust was not decided by diffusion (Nanseu-Njiki et al., 2010). This conclusion was confirmed by Mohammad (2013) that not only diffusion but also others mechanism played roles in the adsorption process of ethoprophos onto apricot stone activated carbon.

El Bakouri et al. (2009) reported that physical forces such as Van der Waals and hydrogen bond were dominant mechanisms and chemical-ion exchange interactions were not responsible in case of drin pesticides adsorption onto acid treated olive stone. The same conclusion was achieved in removing 4–chloro-2-methyl phenoxy acetic acid pesticide by coffee wastes (Al-Zaben and Mekhamer, 2013). Based on the constant adsorption capacity with pH and FTIR results of the adsorbent, the authors suggested that hydrogen bond was a predominant contributor to the adsorption process.

Abdeen and Mohammad (2013) studied ethoprophos elimination by chitosan obtained from shrimp shell, a by-product in food processing industry. The value of energy calculated from Dubinin-Radushkevich isotherm (5.56 kJ/mol) indicated that physical was the mechanism of the adsorption. As FTIR analysis in the research showed the shift of amide and amine group, which might be related to electrostatic interaction between the two groups and negative charge in ethoprophos structure. This finding agrees with previous conclusions conducted by Bhatnagar and Sillanpää (2009) in case of phenol removal by chitin. The authors indicated protonation of functional groups of chitin at low-pH values. In contrast, Li et al. (2009) suggested that not electrostatic interaction but hydrogen bonding, hydrophobic interaction and p–p interaction were the main mechanisms of the adsorption of phenols on functional chitosan. From their study, Nadavala et al. (2009) proposed another mechanism involved the removal of phenol and o-chlorophenol on to chitosan-calcium alginate blended beads is chemical ion-exchange.

4. Application of low-cost biosorbents for SOPs removal from aqueous solutions

Due to their high sorption capacities for organic pollutants and ease of improving modification methods, research on application of biosorbents for SOPs abatement was of increasing concern (Li et al., 2010; Xi and Chen, 2014). Utilisation of biosorbents for removing SOPs including phenol, PAHs, organic pesticides and organic herbicides has been emphasized in recent years.

4.1. Phenolic compounds

Some typical biosorbents such as rice husk, azolla filiculoides, apricot stone shells, tendu leaf, chitin and chitosan were investigated for phenolic compounds removal from water and wastewater (Table 2).

The use of modified rice husk ash for phenol and 2-chrolophenol abatement was studied by Mbui et al. (2002). The biosorbent was created by modifying rice husk with heat. Adsorption results of the material were 0.21mg 2-chlorophenol/g and 14.4 mg phenol/g following Langmuir isotherm. Akhtar et al. (2006) also developed this material by chemically (HNO_3 and CH_3OH) and thermally treated for removing 2,4-dichlorophenol. Optimal conditions for adsorption of 2,4-dichlorophenol was achieved at pH 6, 0.1 g of sorbent/25 mL adsorbate with a concentration of 9.943 mg/L, 10 min contact time, and temperature of 303K. The maximum adsorption properties were obtained from Langmuir and Dubinin- Radushkevich as 156.48 ± 4.89 mg/g (for monolayer) and 407.5 ± 11.41mg/g, respectively.

Results from Nagda et al. (2007) indicated that tendu leaf refuse also is an effective biosorbent to remove phenol from aqueous solution. The maximum adsorption capacities of the raw and modified materials were 7.69 and 31.35 mg/g, respectively. Fruit peels such as banana peel and pomegranate peel also were utilized for eliminating phenolic compounds (Soto et al., 2011; Achak et al., 2009). Values of Qmax for adsorption of 2,4-dichlorophenol on pomegranate peel and phenol on banana peel were 65.7 and 688.9 mg/g, respectively.

Beads of chitosan-calcium alginate were prepared by Nadavala et al. (2009) for phenol and o-chlorophenol removal. The maximum adsorption capacity is achieved around pH 7.0 (o-chlorophenol 97.0 mg/g and phenol 108.6 mg/g) and decreased significantly on either side of pH 7.0. Adsorption process better fitted with Langmuir and Dubinin-Radushkevich isotherms than Freundlich model.

Li et al. (2009) have utilised chitosan and functional chitosan for treating Phenol, p-nitrophenol and p-chlorophenol in the aquatic environment. The adsorption was maximum at pH 7. Raw chitosan has quite limited adsorption efficiency (1.9-2.5 mg/g) while functional chitosan (β-cyclodextrin polymer) and functional chitosan (cross-linked β-cyclodextrin polymer) have much higher adsorption capacities (20.5-179.7 mg/g and 41.1-131.5 mg/g, correspondingly). This biosorbents also can be recovered 6 times for phenol abatement. Kumar et al. (2009) and Kumar et al. (2010) also developed biosorbents from chitosan, chitosan-abrus precatorius and chitosan-coated perlite beads, for the removal of phenolic compounds and achieved very promising results. Maximum adsorption capacities of 2-chlorophenol, 4-chlorophenol and phenol on chitosan-abrus precatorius were 204, 278 and 156 mg/g, respectively and on chitosan-coated perlite beads were 263, 322 and 192 mg/g, respectively.

Prior studies have shown that some biosorbents which have highest phenol adsorption capacities are chitosan-abrus precatorius blended beads, chitosan-coated perlite beads, activated carbons (from apricot stone shells), rice husk ash (acid and heat treated) and banana peel (raw). Maximum removal capacities of low-cost biosorbents for phenolic compounds were equivalent or even higher than those of commercial activated carbon. Moreover, materials exhibited high adsorption capacity for phenolic compounds in both raw and modified forms and adsorption process are best at pH of 7.

Table 2

4.2. Polycyclic aromatic hydrocarbons (PAHs)

Removing some representative kinds of PAHs including phenanthrene, naphthalene, acenaphthene, pyrene, fluorene, anthracene, chrysene, fluoranthene, and perylene from water by biosorbents was researched in this part. Table 3 shows maximum adsorption capacities of biomaterials for typical organic specific pollutants following different models such as Langmuir, Langmuir-Freundlich, Toth, Generalized isotherm.

In a research, Pal (2012) revealed that the adsorption ability of some biosorbents for PAHs followed the order: coconut shell > sugarcane bagasse > rice husk. The adsorption results were in good agreement with Freundlich model. In another study, Chen et al. (2011) has used residue materials including wood chips, ryegrass roots, orange peels, bamboo leaves and pine needles to abate different kinds of PAHs as phenanthrene, naphthalene, acenaphthene, fluorene, pyrene. The results also fitted well with Freudlich isotherm, and the order of PAHs adsorption capacities is pine needles > bamboo leaves > orange peels > ryegrass > wood chips.

Sesame stalk-based carbon was used for removing phenanthrene from water by Kong et al. (2012). The biosorbent was prepared from sesame stalk by carbonization with temperature 300^0C, 400^0C, 500^0C, 600^0C, 700^0C and impregnation with KOH solution. The results showed that surface area of the materials increased with increasing of carbonization temperature from 300^0C (78.32 m^2/g) to 700^0C (274.85 m^2/g). At the phenanthrene concentration of 312.5 mg/L and carbonization temperature 700^0C material, the removal efficiency approaches 100%. Maximum adsorption capacities of the materials following Langmuir-Freudlich and Toth were 383.611 and 420.003 mg/g, respectively.

Xi and Chen (2014) has also used some plant residues including bamboo wood, pine wood, pine needles, pine bark as biosorbents for phenanthrene, naphthalene, acenaphthene and pyrene. This study compared between raw and modified (desugared by HCl solution) materials in terms of efficiency for PAHs elimination. The materials have much higher adsorption capacities after modifying than raw forms. For instance, maximum adsorption value of raw bamboo wood was 1553.88 x10^{-3} mg/g and that of de-sugared bamboo wood was 15865.32 x10^{-3} mg/g.

Another good biosorbents were ultilised for PAHs removal are rice husk (Yakout and Daifullah, 2013) and cork waste (Olivella et al., 2011). Yakout and Daifullah (2013) treated rice husk with H_3PO_4 and heat before using to adsorb phenanthrene, pyrene and naphthalene. Following Langmuir isotherm, the maximum monolayer sorption properties of the biosorbent for these kinds of PAHs are phenanthrene (50.4 mg/g), pyrene (63.6 mg/g) and naphthalene (104.5 mg/g). In their study, Olivella et al. (2011) has used cork waste (raw form) for removing 13 kinds of PAHs (Table 3). This material exhibited medium adsorption capacities for PAHs (monolayer sorption capacities range from (16±3) x10^{-3} to (16±3) x10^{-3} mg/g.

The previous studies found that lignocellulose based biosorbents have much higher PAHs adsorption volume than that of materials prepared from chitin/chitosan. Some of the most promising biosorbents for SOPs abatement are sesame stalk-based carbon, modified rice husk, de-sugared pine wood, de-sugared pine needles and de-sugared bamboo wood. Adsorption capacities of PAHs on biosorbents were much improved after modification while de-sugared method is a very good mean to produce better lignocellulose based materials.

Table 3

4.3. Organic pesticides

Removal of certain types of pesticides such as ethoprophos, oxamyl, DDT and its derivatives, lindane, malathion, aldrin, dieldrin, endrin, 4-chloro-2-methyl phenoxy acetic acid, quinalphos, α-Cypermethrin, methyl parathion, quinalphos, and bromopropylate by biosorbents has also been researched.

Abdeen and Mohammad (2013) used chitosan prepared from shrimp shells to binding Ethoprophos. The shells of shrimp were decalcificated with HCl, deproteinized with NaOH, added $KMnO_4$ and oxalic acid to remove odor and color. Maximum adsorption capacities of the material are 85.47 mg/g (following Langmuir isotherm) and 121.75 mg/g (following Dubinin-Radushkevich isotherm) (Abdeen and Mohammad, 2013).

Apricot stone was also used to create activated carbon for immobilization of organic pesticides. Mohammad (2013) modified the local apricot stone with H_3PO_4 and temperature (500^0C at 2 hours), and HCl to prepare activated carbon for ethoprophos removal. Its maximum monolayer adsorption capacity was 20.04 mg/g. Another study was conducted by Ahmed and Mohammad (2014) produced this material in the same procedure and applied for oxamyl removal from water. The study achieved very good results with maximum monolayer adsorption capacities of activated carbon from apricot stone (147.05 mg/g based on Langmuir isotherm and 121.75 mg/g based on Dubinin-Radushkevich isotherm).

Boussahel et al. (2009) used wood sawdust and cork wastes to abate 4,4-DDT from aqueous solution. The materials were pretreated and sieved to 0.5 mm and 0.2 mm. Maximum adsorption capacities of 4,4-DDT on the materials were significant influenced on the size of the biosorbents. For instance, maximum sorption properties of those biosorbents are wood sawdust (0.5 mm: 4.25 mg/g and 0.2 mm: 69.44 mg/g) and cork wastes (0.5 mm: 2.03 mg/g and 0.2 mm: 19.08 mg/g). The adsorption abilities of 4,4-DDT on the low-cost biosorbents are less than commercial activated carbon (163.9 mg/g).

Coffee waste was used for abating 4-chloro-2-methyl phenoxy acetic acid by Al-Zaben and Mekhamer (2013). The waste was washed and boiled seven times before using for pesticide treatment. The adsorption process did not be affected by pH, and maximum capacity of the material is very high as 340 mg 4-chloro-2-methyl phenoxy acetic acid/g.

In their paper, Ioannidou et al. (2010) prepared activated carbons from corn cob, olive kernel, soya stalks and rapeseed stalks for pesticides adsorption. The biosorbents were produced from agricultural residues by pyrolysis and physical activation. Adsorption isotherms presented that binding capacities of low-cost biosorbents have little less than or equal to that of commercial activated carbons. Maximum adsorption capacities for Bromopropylate of two kinds of commercial activated carbons were Filtrasorb400, Calgon company $15.6x10^{-2}$ mg/g; NORIT® GL50 $21.17x10^{-2}$ mg/g, while that of activated carbons from corn cob, olive kernel, soya stalks, rapeseed stalks were $18.9x10^{-2}$, $12.3x10^{-2}$, $11.6x10^{-2}$, $7.9x10^{-2}$ mg/g, respectively.

As can be seen in Table 4, adsorption capacities of pesticides on biosorbents were often lower than commercial activated carbon. However, biosorbents can be applied for removal of many different kinds of pesticides and several biosorbents have very good binding capacity such as chitosan, activated carbon from apricot stone, acid modified olive stone, coffee wastes and activated carbon from corn cob. Due to differences between natures of various kinds of pesticides, selection of methods to modify materials is different. Pyrolysis and acid treatment are frequently chosen to improve biosorbents.

Table 4

4.4. Organic herbicides

Application of biosorbents for abating some specific organic herbicides such as paraquat, molinate, metribuzin has also been examined by some authors (Table 5). Rice husk was used for removing paraquat by Hsu and Pan (2007). In this study, rice husk was modified with methacrylic acid to produce the biosorbent. Calculation following Langmuir isotherm showed that the biosorbent has a great maximum adsorption capacity for paraquat (317.70 mg/g). Hsu et al. (2009) continued the research with the same procedure for modifying biosorbents, and the result showed that maximum adsorption capacity for paraquat of the material was 292.5 mg/g.

Another biosorbent were also used for binding paraquat is ayous sawdust (Nanseu-Njiki et al., 2010). Adsorption process was significantly affected by pH values. The raise of pH led to increasing of removal efficiency of paraquat on the sawdust. The removal efficiency was 20% at pH 3, while a removal percentage up to 92.6% was achieved at pH 11. Moreover, the adsorbed materials can be reused, and paraquat will be recovered a maximum of 74% when desorption with HCl and HNO_3. The biosorbent has maximum adsorption capacity of paraquat up to 9.47 mg/g.

Ara et al. (2013) ultilised corn cob in the metribuzin treatment from water. Maximum adsorption of metribuzin by the biosorbent was obtained at pH 5, and the Q_{max} value was 4.07 mg/g following Langmuir model. Pine bark was also applied for removing molinate from aqueous solution (Silva et al., 2004). Pine bark was heated overnight at 150^0C in the vacuum environment. Its maximum adsorption capacity following Langmuir isotherm was 10 mg/g. This value is much less than that of activated carbon (113 mg/g) in the research.

Studies in organic herbicide elimination by biosorbents have achieved some very positive results. For example, in those have been examined for paraquat removal, rice husk exhibited its adsorption capacity is much higher than others and even commercial activated carbon. The similar results in case of using chitosan for removing 5-tert-butyl-3-(2,4-dichloro-5-isopropoxyphenyl)-1,3,4-oxadiazol-2(3H)-one from aqueous solution was observed. Techniques such as pyrolysis and acid treatment were also suitable to increase adsorption capacity of biosorbents for organic herbicides.

Table 5

5. Conclusion and future perspectives

Maximum adsorption capacities, efficiency, ease of modification and cost of biosorbents demonstrated that low-cost biosorbents obtained from lignocellulose and chitin/chitosan are high potential for removing SOPs such as phenols, PAHs, organic pesticides, organic herbicides from water. Adsorption mechanisms and capacities depend on the nature of pollutants, characterization and modification methods to produce the adsorbents. Hence, selectivity of suitable biosorbents and modification techniques is crucial and need more attentions. Furthermore, this work also helps to suggest future works in the field of organic pollutant control in water environment.

Lignocellulose and chitin/chitosan can be treated in different ways and for different purposes, such as for production of fuel and fertilizer, for soil conditioning, or just land disposal. Development of low-cost biosorbents will significantly reduce the solid waste volume and serve as a high potential alternative kind of materials for conventional sorbents. Table 6 introduces some potential and obstacles of using biosorbents in SOPs polluted - water treatment.

Table 6

Low-cost biosorbents can be ultilised for eliminating all four main kinds of SOPs including phenols, PAHs, organic pesticides and organic herbicides. Adsorption capacity of the materials could be much improved by suitable modifications. Furthermore, the biomaterials are also much cost effective than commercial carbon. Prices of some typical biosorbents including coconut shell charcoal, rice husk, lignin, chitosan, spheroidal cellulose and cork waste were 0.34, 0.025, 0.06, 2.2 - 15.43, 1.07 and 0.48 (USD.kg^{-1}), respectively (Bhattacharyya and Gupta, 2008; Rafatullah et al., 2010; Olivella et al., 2012). These prices were much cheaper than that of commercial activated carbon (20 USD/kg) (Rafatullah et al., 2010). Based on their cost and removal capacity with different organic compounds, some biosorbents which seem to be attractive for future use such as rice husk, chitosan based materials, sawdust, banana peel, corn grain-based activated carbon, cork waste and coffee waste. Currently, most of the investigations are focused on single or one group of SOPs removal from water. Hence, biosorbents should be experimented for multi polluted water (for instance, multi organic contaminated or heavy metals - organic polluted wastewater). Further work should be carried out to better SOPs adsorption capacity of biosorbents from lignocellulose and chitin/chitosan. As each biosorbents has its merits and demerits, combination of biosorbents can help to improve treatment efficiency. In addition, application of these low-cost materials for SOPs-polluted water treatment is limited and almost at laboratory scale. Hence, large scale study (pilot or full-scale) on the adsorption of biosorbents should be conducted and evaluated in terms of both technical and economic aspects.

References

1. Abdeen Z., Mohammad S.G. 2013. Study of the Adsorption Efficiency of an Eco-Friendly Carbohydrate Polymer for Contaminated Aqueous Solution by Organophosphorus Pesticide. Open J. Org. Polym. Mater.

2. Abdolali, A., Guo, W.S., Ngo, H.H., Chen, S.S., Nguyen, N.C., Tung, K.L., 2014. Typical lignocellulosic wastes and by-products for biosorption process in water and wastewater treatment: A critical review. Bioresour. Technol. 160, 57-66.
3. Achak, M., Hafidi, A., Ouazzani, N., Sayadi, S., Mandi, L., 2009. Low cost biosorbent “banana peel” for the removal of phenolic compounds from olive mill wastewater: Kinetic and equilibrium studies. J. Hazard. Mater. 166, 117-125.
4. Ahmad, T., Rafatullah, M., Ghazali, A., Sulaiman, O., Hashim, R., Ahmad, A., 2010. Removal of pesticides from water and wastewater by different adsorbents: A review. J. Environ. Sci. Health., Part C 28, 231-271.
5. Ahmed, S.M., Mohammad, S.G., 2014. Egyptian apricot stone (Prunus armeniaca) as a low cost and eco-friendly biosorbent for oxamyl removal from aqueous solutions. Am. J. Exp. Agric. 4, 302-321.
6. Akhtar, M., Bhanger, M.I., Iqbal, S., Hasany, S.M., 2006. Sorption potential of rice husk for the removal of 2,4-dichlorophenol from aqueous solutions: Kinetic and thermodynamic investigations. J. Hazard. Mater. 128, 44-52.
7. Aksu, Z., 2005. Application of biosorption for the removal of organic pollutants: a review. Process Biochem. 40, 997-1026.
8. Alam, J.B., Dikshit, A.K., Bandyopadhyay, M., 2000. Efficacy of adsorbents for 2, 4-D and atrazine removal from water environment. Global nest: Int. J. 2, 139-148.
9. Al-Zaben, M.I., Mekhamer, W.K., 2013. Removal of 4-chloro-2-methyl phenoxy acetic acid pesticide using coffee wastes from aqueous solution. Arabian J. Chem.
10. Ara, B., Shah, J., Jan, M.R., Aslam, S., 2013. Removal of metribuzin herbicide from aqueous solution using corn cob. Int. J. Environ. Sci. Technol. 2, 146-161.
11. Arvand, M., Latify, L., Tajmehri, H., Yagubov, A.I., Nuriyev, A.N., Pourhabib, A., Abolhassani, M.R., 2009. Comparative study for the removal of oxadiazon from aqueous solutions by adsorption on chitosan and activated carbon. Anal. Lett. 42, 856-869.
12. Ata, A., Nalcaci, O.O., Ovez, B., 2012. Macro algae Gracilaria verrucosa as a biosorbent: A study of sorption mechanisms. Algal Research 1, 194-204.
13. Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D., 1999. A review of potentially low-cost sorbents for heavy metals. Water Res. 33, 2469-2479.
14. Bhatnagar, A., Sillanpää, M., 2009. Applications of chitin-and chitosan-derivatives for the detoxification of water and wastewater-a short review. Adv. Colloid Interface Sci. 152, 26-38.
15. Bhattacharyya, K.G., Gupta, S.S., 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. Adv. Colloid Interface Sci. 140, 114-131.
16. Boudesocque, S., Guillon, E., Aplincourt, M., Martel, F., Noël, S., 2008. Use of a low-cost biosorbent to remove pesticides from wastewater. J. Environ. Qual. 37, 631-638.
17. Boussahel, R., Irinislimane, H., Harik, D., Moussaoui, K.M., 2009. Adsorption, kinetics, and equilibrium studies on removal of 4, 4-DDT from aqueous solutions using low-cost adsorbents. Chem. Eng. Commun. 196, 1547-1558.
18. Celis, R., Adelino, M.A., Hermosín, M.C., Cornejo, J., 2012. Montmorillonite–chitosan bionanocomposites as adsorbents of the herbicide clopyralid in aqueous solution and soil/water suspensions. J. Hazard. Mater. 209, 67-76.
19. Chen, B., Yuan, M., Liu, H., 2011. Removal of polycyclic aromatic hydrocarbons from aqueous solution using plant residue materials as a biosorbent. J. Hazard. Mater. 188, 436-442.

20. Chingombe, P., Saha, B., Wakeman, R.J., 2006. Effect of surface modification of an engineered activated carbon on the sorption of 2, 4-dichlorophenoxy acetic acid and benazolin from water. J. Colloid Interface Sci. 297, 434-442.
21. Crisafully, R., Milhome, M.A.L., Cavalcante, R.M., Silveira, E.R., De Keukeleire, D., Nascimento, R.F. 2008. Removal of some polycyclic aromatic hydrocarbons from petrochemical wastewater using low-cost adsorbents of natural origin. Bioresour. Technol. 99, 4515-4519.
22. Daifullah, A.A.M., Girgis, B.S., 1998. Removal of some substituted phenols by activated carbon obtained from agricultural waste. Water Res. 32, 1169-1177.
23. Dursun, G., Cicek, H., Dursun, A.Y., 2005. Adsorption of phenol from aqueous solution by using carbonised beet pulp. J. Hazard. Mater. 125, 175-182.
24. El Bakouri, H., Usero, J., Morillo, J., Ouassini, A., 2009. Adsorptive features of acid-treated olive stones for drin pesticides: equilibrium, kinetic and thermodynamic modeling studies. Bioresour. Technol. 100, 4147-4155.
25. Ferraz, A., Baeza, J., Rodriguez, J., Freer, J., 2000. Estimating the chemical composition of biodegraded pine and eucalyptus wood by DRIFT spectroscopy and multivariate analysis. Bioresour. Technol. 74, 201-212.
26. Gupta, V.K., Ali, I., Saini, V.K., 2006. Adsorption of 2, 4-D and carbofuran pesticides using fertilizer and steel industry wastes. J. Colloid Interface Sci. 299, 556-563.
27. Hamadi, N.K., Swaminathan, S., Chen, X.D., 2004. Adsorption of paraquat dichloride from aqueous solution by activated carbon derived from used tires. J. Hazard. Mater. 112, 133-141.
28. Hameed, B.H., Rahman, A.A., 2008. Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material. J. Hazard. Mater. 160, 576-581.
29. Hossain, M.A., Ngo, H.H., Guo, W.S., Setiadi, T., 2012. Adsorption and desorption of copper (II) ions onto garden grass. Bioresour. Technol. 121, 386-395.
30. Hsu, S.T., Chen, L.C., Lee, C.C., Pan, T.C., You, B.X., Yan, Q.F., 2009. Preparation of methacrylic acid-modified rice husk improved by an experimental design and application for paraquat adsorption. J. Hazard. Mater. 171, 465-470.
31. Hsu, S.T., Pan, T.C., 2007. Adsorption of paraquat using methacrylic acid-modified rice husk. Bioresour. Technol. 98, 3617-3621.
32. Ioannidou, O.A., Zabaniotou, A.A., Stavropoulos, G.G., Islam, M.A., Albanis, T.A., 2010. Preparation of activated carbons from agricultural residues for pesticide adsorption. Chemosphere 80, 1328-1336.
33. Islam, M.A., Sakkas, V., Albanis, T.A., 2009. Application of statistical design of experiment with desirability function for the removal of organophosphorus pesticide from aqueous solution by low-cost material. J. Hazard. Mater. 170, 230-238.
34. Ismail, H., Edyham, M.R., Wirjosentono, B., 2002. Bamboo fibre filled natural rubber composites: the effects of filler loading and bonding agent. Polym. Test. 21, 139-144.
35. Jørgensen, H., Kristensen, J.B., Felby, C., 2007. Enzymatic conversion of lignocellulose into fermentable sugars: challenges and opportunities. Biofuels, Bioprod. Biorefin. 1, 119-134.
36. Kalderis, D., Koutoulakis, D., Paraskeva, P., Diamadopoulos, E., Otal, E., Valle, J.O.D., Fernández-Pereira, C., 2008. Adsorption of polluting substances on activated carbons prepared from rice husk and sugarcane bagasse. Chem. Eng. J. 144, 42-50.

37. Khalil, H.S.A., Alwani, M.S., Omar, A.K.M., 2007. Chemical composition, anatomy, lignin distribution, and cell wall structure of Malaysian plant waste fibers. BioResources, 1, 220-232.
38. Khiari, R., Mhenni, M.F., Belgacem, M.N., Mauret, E., 2010. Chemical composition and pulping of date palm rachis and Posidonia oceanica - a comparison with other wood and non-wood fibre sources. Bioresour. Technol. 101, 775-780.
39. Kong, H., He, J., Wu, H., Wu, H., Gao, Y., 2012. Phenanthrene Removal from Aqueous Solution on Sesame Stalk-based Carbon. CLEAN–Soil, Air, Water 40, 752-759.
40. Krishnani, K.K., Meng, X., Christodoulatos, C., Boddu, V.M., 2008. Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. J. Hazard. Mater. 153, 1222-1234.
41. Kumar, N.S., Venkata Subbaiah, M., Subba Reddy, A., Krishnaiah, A., 2009. Biosorption of phenolic compounds from aqueous solutions onto chitosan–abrus precatorius blended beads. J. Chem. Technol. Biotechnol. 84, 972-981.
42. Kumar, N.S., Suguna, M., Subbaiah, M.V., Reddy, A.S., Kumar, N.P., Krishnaiah, A., 2010. Adsorption of phenolic compounds from aqueous solutions onto chitosan-coated perlite beads as biosorbent. Ind. Eng. Chem. Res. 49, 9238-9247.
43. Li, J.M., Meng, X.G., Hu, C.W., Du, J., 2009. Adsorption of phenol, chlorophenol and nitrophenol onto functional chitosan. Bioresour. Technol. 100, 1168-1173.
44. Li, Q., Su, H., Tan, T., 2008. Synthesis of ion-imprinted chitosan-TiO_2 adsorbent and its multi-functional performances. Biochem. Eng. J. 38, 212-218.
45. Li, Y., Chen, B., Zhu, L., 2010. Enhanced sorption of polycyclic aromatic hydrocarbons from aqueous solution by modified pine bark. Bioresour. Technol. 101, 7307-7313.
46. Liu, Q.S., Zheng, T., Wang, P., Jiang, J.P., Li, N., 2010. Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers. Chem. Eng. J. 157, 348-356.
47. Mbui, D.N., Shiundu, P.M., Ndonye, R.M., Kamau, G.N. 2002. Adsorption and detection of some phenolic compounds by rice husk ash of Kenyan origin. J. Environ. Monit. 4, 978-984.
48. Mohammad, S.G., 2013. Biosorption of Pesticide Onto a Low Cost Carbon Produced from Apricot Stone (Prunus armeniaca): Equilibrium, Kinetic and Thermodynamic Studies. J. Appl. Sci. Res. 9, 6459-6469.
49. Moreno, R.F., López, C.J., Galvín, M.R., Cordón, M.M., Mellado, R.J., 2010. On the removal of s-triazine herbicides from waters using commercial low-cost granular carbons. J. Serb. Chem. Soc. 75, 405-412.
50. Nadavala, S.K., Swayampakula, K., Boddu, V.M., Abburi, K., 2009. Biosorption of phenol and o-chlorophenol from aqueous solutions on to chitosan–calcium alginate blended beads. J. Hazard. Mater. 162, 482-489.
51. Nagda, G.K., Diwan, A.M., Ghole, V.S., 2007. Potential of tendu leaf refuse for phenol removal in aqueous systems. Appl. Ecol. Env. Res. 5, 1-9.
52. Nalcaci, O.O., Böke, N., Ovez, B., 2011. Comparative Study on the Removal of Various Phenoxyalkanoic Acid Herbicides from Aqueous Solutions on Polycaprolactone and Activated Carbon. J. Environ. Eng. 137, 1136-1144.
53. Nanseu-Njiki, C.P., Dedzo, G.K., Ngameni, E., 2010. Study of the removal of paraquat from aqueous solution by biosorption onto Ayous Triplochiton schleroxylon sawdust. J. Hazard. Mater. 179, 63-71.

54. Nguyen, T.A.H., Ngo, H.H., Guo, W.S., Zhang, J., Liang, S., Yue, Q.Y., Nguyen, T.V., 2013. Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. Bioresour. Technol. 148, 574-585.
55. Olivella, M.À., Fernández, I., Cano, L., Jové, P., Oliveras, A., 2012. Role of chemical components of cork on sorption of aqueous polycyclic aromatic hydrocarbons. Int. J. Environ. Res. 7, 225-234.
56. Olivella, M.A., Jove, P., Oliveras, A., 2011. The use of cork waste as a biosorbent for persistent organic pollutants-study of adsorption/desorption of polycyclic aromatic hydrocarbons. J. Environ. Sci. Health., Part A 46, 824-832.
57. Olivella, M.À., Jové, P., Bianchi, A., Bazzicalupi, C., Cano, L., 2013. An integrated approach to understanding the sorption mechanism of phenanthrene by cork. Chemosphere 90, 1939-1944.
58. Pal, D., 2012. Adsorption of polycyclic aromatic hydrocarbons using agricultural wastes-effect of lignin content. ene 14, 4-57.
59. Park, K.H., Balathanigaimani, M.S., Shim, W.G., Lee, J.W., Moon, H., 2010. Adsorption characteristics of phenol on novel corn grain-based activated carbons. Microporous Mesoporous Mater. 127, 1-8.
60. Pham T.T., Nguyen A.V., Van der Bruggen B., 2012. Evaluation of Two Low-Cost–High-Performance Adsorbent Materials in the Waste-to-Product Approach for the Removal of Pesticides from Drinking Water. CLEAN–Soil, Air, Water 40, 246-253.
61. Rafatullah, M., Sulaiman, O., Hashim, R., Ahmad, A., 2010. Adsorption of methylene blue on low-cost adsorbents: a review. J. Hazard. Mater. 177, 70-80.
62. Ravi Kumar, M.N., 2000. A review of chitin and chitosan applications. React. Funct. Polym. 46, 1-27.
63. Sathishkumar, M., Vijayaraghavan, K., Binupriya, A.R., Stephan, A.M., Choi, J.G., Yun, S.E., 2008. Porogen effect on characteristics of banana pith carbon and the sorption of dichlorophenols. J. Colloid Interface Sci. 320, 22-29.
64. Silva, M., Fernandes, A., Mendes, A., Manaia, C.M., Nunes, O.C., 2004. Preliminary feasibility study for the use of an adsorption/bio-regeneration system for molinate removal from effluents. Water Res. 38, 2677-2684.
65. Soto, M.L., Moure, A., Domínguez, H., Parajó, J.C., 2011. Recovery, concentration and purification of phenolic compounds by adsorption: a review. J. Food Eng. 105, 1-27.
66. Srivastava, B., Jhelum, V., Basu, D.D., Patanjali, P.K., 2009. Adsorbents for pesticide uptake from contaminated water: a review. J Sci Ind Res. 68, 839-850.
67. Srivastava, V.C., Swamy, M.M., Mall, I.D., Prasad, B., Mishra, I.M., 2006. Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamics. Colloids Surf., A 272, 89-104.
68. Valili, S., Siavalas, G., Karapanagioti, H.K., Manariotis, I.D., Christanis, K., 2013. Phenanthrene removal from aqueous solutions using well-characterized, raw, chemically treated, and charred malt spent rootlets, a food industry by-product. J. Environ. Manage 128, 252-258.
69. Wang, S.L., Tzou, Y.M., Lu, Y.H., Sheng, G., 2007. Removal of 3-chlorophenol from water using rice-straw-based carbon. J. Hazard. Mater. 147, 313-318.
70. Xi, Z., Chen, B., 2014. Removal of polycyclic aromatic hydrocarbons from aqueous solution by raw and modified plant residue materials as biosorbents. J. Environ. Sci. (China) 26, 737-748.

71. Yakout, S.M., Daifullah, A.A.M., 2013. Removal of selected polycyclic aromatic hydrocarbons from aqueous solution onto various adsorbent materials. Desalin. Water Treatment 51, 6711-6718.
72. Zolgharnein, J., Shahmoradi, A., Ghasemi, J., 2011. Pesticides Removal Using Conventional and Low-Cost Adsorbents: A Review. Clean–Soil, Air, Water 39, 1105-1119.

FIGURE CAPTIONS

Fig. 1. Average chemical composition of some typical lignocellulose (% dry weight)

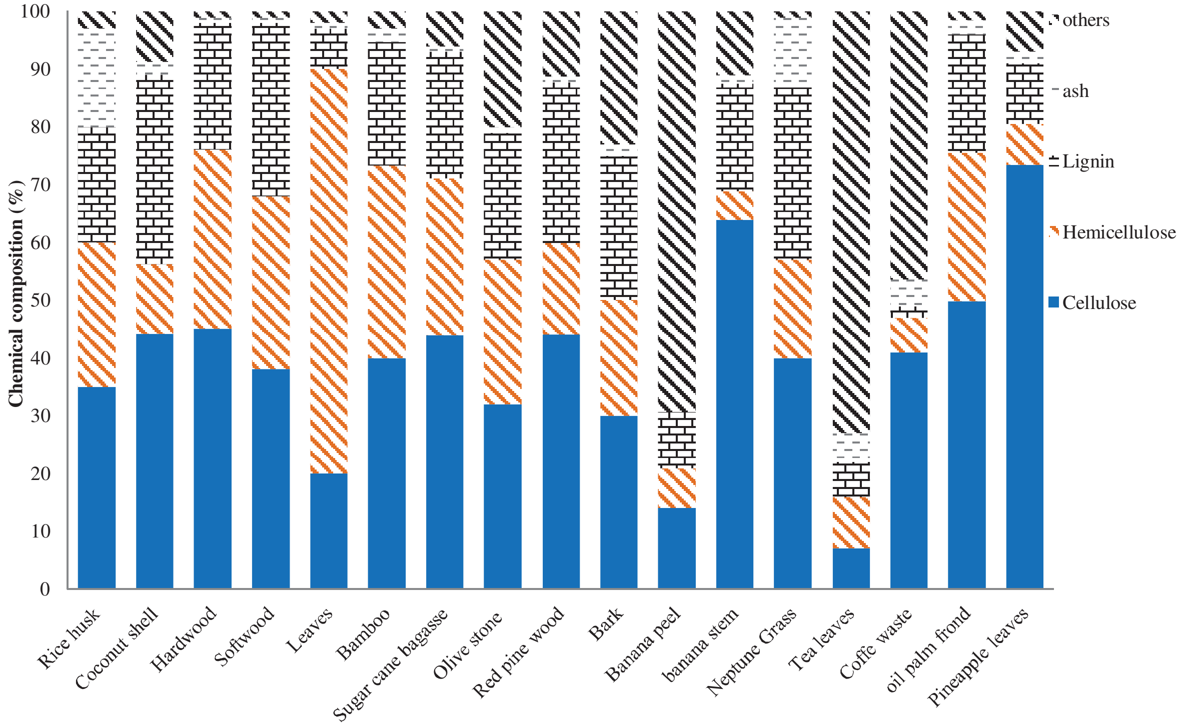
Chemical composition (%)
0
10
20
30
40
50
60
70
80
90
100
Rice husk
Coconut shell
Hardwood
Softwood
Leaves
Bamboo
Sugar cane bagasse
Olive stone
Red pine wood
Bark
Banana peel
banana stem
Neptune Grass
Tea leaves
Coffe waste
oil palm frond
Pineapple leaves
others
ash
Lignin
Hemicellulose
Cellulose

Fig. 1

TABLES

Table 1

Summary of characteristics of biosorbents from lignocellulose and chitin/chitosan

Characteristics	Lignocellulose	Chitin/chitosan
Chemical composition/chemical structure	Cellulose: 7-73%; hemicellulose: 6-33%; lignin: 2-33%; ash: 1-17%; others: 1-69%	Chitin: 2-acetamido-2-deoxy-β-D-glucose; Chitosan: polymer of D-glucosamine and N-acetyl-D-glucosamine units
Functional groups	(-OH), (-COOH), (Si-OH), alkyne, aromatic rings, ketone, aldehydes, lactones	(-OH), ($-NH_3^+$), ($-CH_2COOH$), (-COOH), (C=O) of acetyl, amide ($-CONH_2$)
Surface area and porosity	Raw form: 3.41 - 25.97 m^2/g; modified form: 566 m^2/g	Pure chitosan: 0.654 m^2/g; beads of chitosan-sodium alginate: 102.15m^2/g

Table 2
Phenolic compounds adsorption capacity of raw/modified biosorbents

Adsorbate	Adsorbents (modifying agent)	Isotherms	Q_{max} (mg/g)	Source
2-chlorophenol	Rice husk (heat treated)	Langmuir	0.21[a]	Mbui et al., 2002
	Chitosan–abrus precatorius blended beads	Langmuir	204	Kumar et al., 2009
	Chitosan-coated perlite beads	Langmuir	263[m]	Kumar et al., 2010
	Activated carbon fibers	Langmuir	245.29[a]	Liu et al., 2010
4-chlorophenol	Chitosan–abrus precatorius blended beads	Langmuir	278	Kumar et al., 2009
	Chitosan-coated perlite beads	Langmuir	322[m]	Kumar et al., 2010
	Activated carbon fibers	Langmuir	242.46[a]	Liu et al., 2010
o-chlorophenol	Beads of chitosan (sodium alginate, $CaCl_2$)	Langmuir	97.0	Nadavala et al., 2009
2,4-dichlorophenol	Activated carbons (from apricot stone shells)	Langmuir	339	Daifullah and Girgis, 1998
	Activated carbon fibers	Langmuir	367.4[a]	Liu et al., 2010
	Pomegranate peel	Langmuir	65.7	Soto et al., 2011
	Rice husk ash (HNO_3, CH_3OH and heat treated)	Langmuir	156.48 ± 4.89[ma]	Akhtar et al., 2006
	Rice husk ash (HNO_3, CH_3OH and heat treated)	Dubinin-Radushkevich	407.5 ± 11.41[a]	Akhtar et al., 2006
2,4,6-trichlorophenol	Activated carbon fibers	Langmuir	479.8[a]	Liu et al., 2010
	Rice-straw-based carbon	Langmuir	14.2	Wang et al., 2007
4-nitrophenol	Activated carbon fibers	Langmuir	313.97[a]	Liu et al., 2010
2,4-dinitrophenol	Activated carbons (from apricot stone shells)	Langmuir	232	Daifullah and Girgis, 1998
	Activated carbon fibers	Langmuir	418.29[a]	Liu et al., 2010
Phenol	Rice husk (heat treated)	Langmuir	14.4[a]	Mbui et al., 2002
	Tendu leaf refuse (raw)	Langmuir	7.6923	Nagda et al., 2007
	Tendu leaf refuse (H_2SO_4, heat treated)	Langmuir	31.348	Nagda et al., 2007
	Chitin	Langmuir	21.5	Bhatnagar and Sillanpää, 2009
	Beads of chitosan (sodium alginate, $CaCl_2$)	Langmuir	108.6	Nadavala et al., 2009
	Commercial activated carbon	Langmuir	30.2	Srivastava et al., 2006
	Commercial activated carbon	Toth	47.73	Srivastava et al., 2006
	Chitosan–abrus precatorius blended beads	Langmuir	156	Kumar et al., 2009
	Chitosan-coated perlite beads	Langmuir	192[m]	Kumar et al., 2010
	Activated carbon derived from rattan sawdust	Langmuir	149.25	Hameed and Rahman, 2008
	Activated carbon derived from rattan sawdust	Dubinin-Radushkevich	122.99	Hameed and Rahman, 2008
	Activated carbon fibers	Langmuir	110.2[a]	Liu et al., 2010
	Carbonized beet pulp	Langmuir	89.96	Dursun et al., 2005
	Rice husk activated carbon	Langmuir	27.58	Kalderis et al., 2008
	Carbon from banana pith	Langmuir	129.4	Sathishkumar et al., 2008
	Banana peel (raw)	Langmuir	688.9	Achak et al.,

				2009
	corn grain-based activated carbon	Langmuir	256	Park et al., 2010
Phenol, p-nitrophenol and p-chlorophenol	Chitosan	Langmuir	1.9-2.5	Li et al., 2009
	Functional chitosan (β-cyclodextrin polymer)	Langmuir	20.5-179.7	Li et al., 2009
	Functional chitosan (cross-linked β-cyclodextrin polymer)	Langmuir	41.1-131.5	Li et al., 2009
Nonylphenol	Chitosan	Langmuir	56.3	Soto et al., 2011

^{m}: monolayer sorption capacity; ^{a}: unit mmol/gram is converted into mg/g for comparison purpose

Table 3

PAHs adsorption capacity of raw/modified biosorbents

Adsorbate	Adsorbents (modifying agent)	Isotherms	Q_{max} (mg/g)	Source
Total PAHs	Green coconut shell	Not given	0.553	Crisafully et al., 2008
	Sugar cane bagasse	Not given	0.345	Crisafully et al., 2008
	Chitin	Not given	0.215	Crisafully et al., 2008
	Chitosan	Not given	0.112	Crisafully et al., 2008
Phenanthrene	Bamboo wood (raw)	Langmuir	1553.88 x10^{-3}	Xi and Chen, 2014
	Bamboo wood (de-sugared)	Langmuir	15865.32 x10^{-3}	Xi and Chen, 2014
	Pine wood (raw)	Langmuir	2318.05 x10^{-3}	Xi and Chen, 2014
	Pine wood (de-sugared)	Langmuir	15866.5 x10^{-3}	Xi and Chen, 2014
	Pine needles (raw)	Langmuir	2277.22 x10^{-3}	Xi and Chen, 2014
	Pine needles (de-sugared)	Langmuir	15403.15 x10^{-3}	Xi and Chen, 2014
	Pine bark (raw)	Langmuir	2127.32 x10^{-3}	Xi and Chen, 2014
	Pine bark (de-sugared)	Langmuir	13824.85 x10^{-3}	Xi and Chen, 2014
	Cork waste (raw)	Langmuir	(32±5)x10^{-3} [m]	Olivella et al., 2011
	Sesame stalk-based carbon	Langmuir	19.008 [m]	Kong et al., 2012
	Sesame stalk-based carbon	Langmuir-Freundlich	383.611	Kong et al., 2012
	Sesame stalk-based carbon	Toth	420.003	Kong et al., 2012
	Rice husk (H_3PO_4, heat)	Langmuir	50.4 [m]	Yakout and Daifullah, 2013
	Rice husk (H_3PO_4, heat)	Toth	39.4 [m]	Yakout and Daifullah, 2013
	Rice husk (H_3PO_4, heat)	Generalized isotherm	216.0 [m]	Yakout and Daifullah, 2013
Naphthalene	Pine wood (raw)	Langmuir	2820.61 x10^{-3}	Xi and Chen, 2014
	Pine wood (de-sugared)	Langmuir	18902.99 x10^{-3}	Xi and Chen, 2014
	Pine needles (raw)	Langmuir	2635.76 x10^{-3}	Xi and Chen, 2014
	Pine needles (de-sugared)	Langmuir	18068.64 x10^{-3}	Xi and Chen, 2014
	Rice husk (H_3PO_4, heat)	Langmuir	63.6 [m]	Yakout and Daifullah, 2013
	Rice husk (H_3PO_4, heat)	Toth	86.9 [m]	Yakout and Daifullah, 2013
	Rice husk (H_3PO_4, heat)	Generalized isotherm	14.8 [m]	Yakout and Daifullah, 2013
Acenaphthene	Pine wood (raw)	Langmuir	1497.9 x10^{-3}	Xi and Chen, 2014
	Pine wood (de-sugared)	Langmuir	7533.47 x10^{-3}	Xi and Chen, 2014
	Pine needles (raw)	Langmuir	1597.8 x10^{-3}	Xi and Chen, 2014
	Pine needles (de-sugared)	Langmuir	7106.92 x10^{-3}	Xi and Chen, 2014
	Cork waste (raw)	Langmuir	(46±25)x10^{-3} [m]	Olivella et al., 2011
Pyrene	Pine wood (raw)	Langmuir	417.7 x10^{-3}	Xi and Chen, 2014
	Pine wood (de-sugared)	Langmuir	3084.4 x10^{-3}	Xi and Chen, 2014
	Pine needles (raw)	Langmuir	447.56 x10^{-3}	Xi and Chen, 2014
	Pine needles (de-sugared)	Langmuir	3103.27 x10^{-3}	Xi and Chen, 2014
	Cork waste (raw)	Langmuir	(32±4)x10^{-3} [m]	Olivella et al., 2011
	Rice husk (H_3PO_4, heat)	Langmuir	104.5 [m]	Yakout and

				Daifullah, 2013
	Rice husk (H_3PO_4, heat)	Toth	109.3^{m}	Yakout and Daifullah, 2013
	Rice husk (H_3PO_4, heat)	Generalized isotherm	16.9^{m}	Yakout and Daifullah, 2013
Benzo(a)pyrene	Cork waste (raw)	Langmuir	$(21\pm5)x10^{-3\ m}$	Olivella et al., 2011
Indeno(1,2,3-cd)pyrene	Cork waste (raw)	Langmuir	$(20\pm18)x10^{-3\ m}$	Olivella et al., 2011
Fluorene	Cork waste (raw)	Langmuir	$(49\pm26)x10^{-3\ m}$	Olivella et al., 2011
Anthracene	Cork waste (raw)	Langmuir	$(26\pm18)x10^{-3\ m}$	Olivella et al., 2011
Dibenz(a,h)anthracene	Cork waste (raw)	Langmuir	$(16\pm3)x10^{-3\ m}$	Olivella et al., 2011
Benz(a)anthracene	Cork waste (raw)	Langmuir	$(26\pm8)x10^{-3\ m}$	Olivella et al., 2011
Chrysene	Cork waste (raw)	Langmuir	$(23\pm5)x10^{-3\ m}$	Olivella et al., 2011
Benzo(b)fluoranthene	Cork waste (raw)	Langmuir	$(28\pm12)x10^{-3\ m}$	Olivella et al., 2011
Benzo(k)fluoranthene	Cork waste (raw)	Langmuir	$(21\pm7)x10^{-3\ m}$	Olivella et al., 2011
Benzo(ghi)perylene	Cork waste (raw)	Langmuir	$(23\pm2)x10^{-3\ m}$	Olivella et al., 2011

^{m}: monolayer sorption capacity

Table 4
Organic pesticides adsorption capacity of raw/modified biosorbents

Adsorbate	Adsorbents (modifying agent)	Isotherms	Q_{max} (mg/g)	Source
Ethoprophos	Chitosan prepared from shrimp shells	Langmuir	85.47	Abdeen and Mohammad, 2013
	Chitosan prepared from shrimp shells	Dubinin-Radushkevich	121.75	Abdeen and Mohammad, 2013
	Activated carbons from Apricot stone	Langmuir	20.04^{m}	Mohammad, 2013
Oxamyl	Activated carbons from Apricot stone	Langmuir	147.05^{m}	Ahmed and Mohammad, 2014
	Activated carbons from Apricot stone	Dubinin-Radushkevich	121.75^{m}	Ahmed and Mohammad, 2014
4,4-DDT	Wood sawdust	Langmuir	4.25-69.44	Boussahel et al., 2009
	Cork wastes	Langmuir	2.03-19.08	Boussahel et al., 2009
	Commercial activated carbon	Langmuir	163.9	Boussahel et al., 2009
DDD	Bagasse fly ash	Langmuir	$7.69x10^{-3}$	Zolgharnein et al., 2011
DDE	Bagasse fly ash	Langmuir	$6.67x10^{-3}$	Zolgharnein et al., 2011
Lindane	Bagasse fly ash	Langmuir	$2.51x10^{-3}$	Zolgharnein et al., 2011
Malathion	Bagasse fly ash	Langmuir	$2.08x10^{-3}$	Zolgharnein et al., 2011
Aldrin	Olive stone (acid-treated)	Langmuir	$19.54x10^{-3}$	Zolgharnein et al., 2011
Dieldrin	Olive stone (acid-treated)	Langmuir	23.74	Zolgharnein et al., 2011
Endrin	Olive stone (acid-treated)	Langmuir	43.71	Zolgharnein et al., 2011
4-chloro-2-methyl phenoxy acetic acid	Coffee wastes	Langmuir	340	Al-Zaben and Mekhamer, 2013
Quinalphos	Used tea leaves	Langmuir	$196.07x10^{-3}$	Islam et al., 2009
α-Cypermethrin	Cork	Langmuir	$303x10^{-3}$	Ahmad et al., 2010
Methyl parathion	Rice bran	Langmuir	113.59 ± 2.62^{a}	Ahmad et al., 2010
Methyl parathion	Rice husk	Langmuir	101.94 ± 2.33^{a}	Ahmad et al., 2010
Bromopropylate	Activated carbon from corn cob	Langmuir	$18.9x10^{-2}$	Ioannidou et al., 2010
	Activated carbon from olive kernel	Langmuir	$12.3x10^{-2}$	Ioannidou et al., 2010
	Activated carbon from soya stalks	Langmuir	$11.6x10^{-2}$	Ioannidou et al., 2010
	Activated carbon from rapeseed stalks	Langmuir	$7.9x10^{-2}$	Ioannidou et al., 2010
	Commercial activated carbon (Filtrasorb400, Calgon company)	Langmuir	$15.6x10^{-2}$	Ioannidou et al., 2010
	Commercial activated carbon (NORIT® GL50)	Langmuir	$21.17x10^{-2}$	Ioannidou et al., 2010

^{m}: monolayer sorption capacity; ^{a}: unit mmol/gram is converted into mg/g for comparison purpose

Table 5
Organic herbicides adsorption capacity of raw/modified biosorbents

Adsorbate	Adsorbents (modifying agent)	Isotherms	Q_{max} (mg/g)	Source
Paraquat	Rice husk (methacrylic acid)	Langmuir	292.5	Hsu et al., 2009
	Ayous sawdust	Langmuir	9.47	Nanseu-Njiki et al., 2010
	Rice husk (methacrylic acid)	Langmuir	317.70	Hsu and Pan, 2007
	Commercial activated carbon	Langmuir	75.80	Hamadi et al., 2004
	Commercial activated carbon	Langmuir	90	Hsu and Pan, 2007
Molinate	Pine bark (heat)	Langmuir	10	Silva et al., 2004
	Activated carbon	Langmuir	113	Silva et al., 2004
Metribuzin	Corn cob	Langmuir	4.07	Ara et al., 2013
Isoproturon	Lignocellulosic substrate	Langmuir	61.8	Boudesocque et al., 2008
Terbumeton	Lignocellulosic substrate	Langmuir	11.2	Boudesocque et al., 2008
Prometon	Vegetable activated carbon	Langmuir	23.51	Moreno et al., 2010
	Mineral activated carbon	Langmuir	24.58	Moreno et al., 2010
	Coconut activated carbon	Langmuir	26.02	Moreno et al., 2010
Propazine	Vegetable activated carbon	Langmuir	25.62	Moreno et al., 2010
	Mineral activated carbon	Langmuir	25.05	Moreno et al., 2010
	Coconut activated carbon	Langmuir	27.15	Moreno et al., 2010
Prometryn	Vegetable activated carbon	Langmuir	23.92	Moreno et al., 2010
	Mineral activated carbon	Langmuir	24.75	Moreno et al., 2010
	Coconut activated carbon	Langmuir	26.32	Moreno et al., 2010
2,4-D	Commercial activated carbon (AC F400)	Langmuir	8.13-10.48[a]	Chingombe et al., 2006
	Surface modified activated carbon (AC F400AN)	Langmuir	11.76-16.25[a]	Chingombe et al., 2006
	Wood charcoal	Freundlich	0.7	Alam et al., 2000
	Standard activated charcoal	Not given	303.3	Gupta et al., 2006
Atrazine	Wood charcoal	Freundlich	0.8	Alam et al., 2000
5-tert-butyl-3-(2,4-dichloro-5-isopropoxyphenyl)-1,3,4-oxadiazol-2(3H)-one	Chitosan	Langmuir	5.02	Arvand et al., 2009
	Activated carbon	Langmuir	4.32	Arvand et al., 2009

[m]: monolayer sorption capacity; [a]: unit mmol/gram is converted into mg/g for comparison purpose

Table 6
Potentials and obstacles of using biosorbents for SOPs removal from water

Potentials	Obstacles
• Reduce solid waste • Availability in large amount and cheap price of biosorbents, • Modification methods to produce better biosorbents are available, easy to carry out and inexpensive • High uptake capacity for all four kinds of SOPs: phenolic compounds, PAHs, organic pesticides and organic herbicides • Easy for operation, maintenance of the treatment system • Good regeneration ability of biosorbents	• Not much studies on multi SOPs-polluted water or real wastewater • Lack of feasible research on commercialization of this source of materials • Stability of biosorbents in different conditions of real wastewater was not sufficiently understood • Lack of policy to support using biosorbents for wastewater treatment

Highlights

- Characteristics of lignocellulosic sorbents and chitin/chitosan were analysed.
- Uptake mechanism of SOPs was revealed and discussed.
- Modification methods to enhance biosorbents were presented.
- Application of typical low-cost biosorbents to remove SOPs was assessed.
- Future viewpoint to use inexpensive biomaterials for SOPs elimination was proposed.