

## Typical Lignocellulosic Wastes and By-products for Biosorption Process in Water and Wastewater Treatment: A Critical Review

A. Abdolali<sup>a</sup>, W. S. Guo<sup>a</sup>, H. H. Ngo<sup>a\*</sup>, S. S. Chen<sup>b</sup>, N. C. Nguyen<sup>b</sup>, K. L. Tung<sup>c</sup>

<sup>a</sup>Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering,  
University of Technology, Sydney, Broadway, NSW 2007, Australia

<sup>b</sup>Institute of Environmental Engineering and Management, National Taipei University of Technology,  
Taipei 10608, Taiwan

<sup>c</sup>Department of Chemical Engineering, National Taiwan University, Taipei, 10617, Taiwan

\* Corresponding author: School of Civil and Environmental Engineering, University of Technology,  
Sydney (UTS), P.O. Box 123, Broadway, NSW 2007, Australia. Tel.: +61 2 9514 2745; Fax: +61 2 9514  
2633. E-mail address: ngohuuhaol21@gmail.com

### ABSTRACT

Biosorption on lignocellulosic wastes and by-products has been identified as a proper alternative to the existing technologies applied for toxic metal ion and dye removal from wastewater streams. This paper 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. The efficiency of each biosorbent has been also discussed with respect to the operating conditions (e.g. temperature, hydraulic residence time, initial metal concentration, biosorbent particle size and its dosage), chemical modification on sorption capacity and preparation methods, as well as thermodynamics and kinetics.

Keywords: Heavy metals; Biosorption; Low cost biosorbent; Lignocellulosic wastes

## 1 Introduction

In recent decades, industrial activity growth and increasing water usage worldwide have led to the release of various pollutants into aquatic environment, such as toxic heavy metals, dyes, organic compounds like phenols, dyes, pesticides, humic substances, detergents and other persistent organic pollutants.

These kinds of pollutants are mainly characterised by marked not only persistence against chemical or biological degradation, but also high environmental mobility and strong tendency for bioaccumulation in the food chain. A number of treatment methods (e.g. reverse osmosis (RO), filtration, adsorption, chemical precipitation, coagulation, electroplating, evaporation, oxidation/reduction, ion exchange, activated sludge, aerobic and anaerobic treatment, electrolysis, magnetic separation, etc.) have been used to removal the pollutants (Bhatnagar and Sillanpää , 2010; Miretzky and Cirelli, 2010; Crini, 2006). However, most of the existing technologies are often ineffective, uneconomical or very technically complicated when the target heavy metals concentration falls below 100 mg/L. Additionally, some methods also have disadvantages of high reagent usage, high energy requirements and toxic secondary sludge production.

At present, the interests in utilization of cheap alternatives have been significantly increased and many attempts have been made by researchers on feasibility of biosorption potential of lignocellulosic materials (either natural substances or agro-industrial wastes and by-products) as economic and eco-friendly options. Generally,

biosorption processes can significantly reduce capital costs, operational costs and total treatment costs compared with the conventional systems (Bulut and Tez, 2007).

Nevertheless, the lignocellulosic materials have some negative sides such as low uptake capacity in raw form and releasing organic components in terms of high chemical oxygen demand (COD), biological oxygen demand (BOD) and total organic carbon (TOC). Thus, they can cause secondary pollution and oxygen reduction in water (Wan Ngah and Hanafiah, 2008). Many investigations have been carried out to improve the properties of the adsorbents and increase their capacity for metal ion uptake by chemically modification with mineral/organic acids, bases, organic compounds and oxidation agents (e.g. NaOH, CaO, CaCl<sub>2</sub>, citric acid, acetic acid, formaldehyde, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, EDTA, methanol, etc.) (Velazquez-Jimenez et al., 2013; Wan Ngah and Hanafiah, 2008). The pre-treatments could modify the surface characteristics either by removing or masking the functional groups or by exposing more binding sites (Pehlivan et al., 2012). The main parameters influencing pollutants removal are pH value of solution. The range of optimum pH of different lignocellulosic biosorbent is shown in Figure A.1 in Appendix A, initial concentration (as driving force), biomass dose, temperature and contact time. This literature review provides recent studies on low-cost lignocellulosic adsorbents for wastewater treatment, which focused on property modifications of different types of biosorbent lignocellulosic wastes from different industries, their kinetic and thermodynamic studies, as well as the applications for heavy metal ions, dyes, organic and nutrient pollutants removal.

## 2 Characterization of lignocellulosic materials

Lignocellulosic materials have been called photomass because they are a result of photosynthesis. There are several types of cellulose in the cell wall of lignocellulosic materials. Cellulose (30-50%) is a linear polymer of  $\beta$ -D-glucopyranose sugar units whose average chain has a degree of polymerization of about 9,000-10,000 units. Approximately 65% of the cellulose is highly oriented and crystalline with no accessibility to water and other solvents, while the rest is composed of less oriented chains which have association with hemicellulose (20-40%) and lignin (15-25%). Hence, as its partial accessibility to water and other solvents, the molecular structure of cellulose gives a variety of characteristics such as hydrophilicity, chirality and degradability. Moreover, chemical reactivity is strongly a function of the high donor reactivity of the OH groups in cellulose molecules. With lower degree of polymerization than cellulose, the hemicellulose includes a group of polysaccharide polymers and the hemicelluloses which are not crystalline vary in structure and polymer composition depending on the source. Lignins are highly branched without crystalline-structure and are composed of nine carbon units derived from substituted cinnamyl alcohol of which the structure and chemical composition are a function of their source. There are also small amounts of water, ash, cyclic hydrocarbons, organic and inorganic materials presented in lignocellulosic sources as extractives which contains a large number of both lipophilic and hydrophilic constituents (Cagnon et al., 2009; O'Connell et al., 2008). Chemical composition of some common lignocellulosic materials is presented in Table 1. **Table 1**

The type of functional groups and chemical components in lignocellulosic wastes and by-products are similar but in different amounts. They play an important role in heavy metal ions sorption (Asadi et al., 2008). Additionally, in order to enhance and reinforce the functional group potential and increase the number of active sites, some pre-treatment methods using different kinds of modifying agents are applied within known protocols (Bhatnagar and Sillanpää, 2010; Wan Ngah and Hanafiah, 2008). As the agents include organic and mineral acids (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, acetic acid, citric acid and formic acid), bases and basic solutions (NaOH, Na<sub>2</sub>CO<sub>3</sub>, Ca(OH)<sub>2</sub> and CaCl<sub>2</sub>), oxidizing agents (H<sub>2</sub>O<sub>2</sub> and K<sub>2</sub>MnO<sub>4</sub>) and many other mineral and organic chemical compounds (formaldehyde, glutaraldehyde, CH<sub>3</sub>OH, poly ethylene imine and epichlorohydrin).

According to the research carried out by O’Cannell et al. (2008), chemical modification can be applied to change certain properties of lignocellulosic biosorbents such as hydrophilic or hydrophobic characters, elasticity, water sorption ability, adsorptive or ion exchange capability, resistance to microbiological attack and thermal resistance. In fact, chemical modification conducts two main approaches to enhance biosorptive capabilities: 1) the direct modification of the molecular structure through the introduction of chelating or metal binding functionalities through esterification (e.g. succinic anhydride and citric acid), etherification (e.g. sodium methylate, epichlorohydrin and polyethyleneimine), halogenation (e.g. 3-mercaptopropionic acid) and oxidation (e.g. sodium metaperiodate); and 2) grafting of selected monomers and adding to main chain of polymers so as to directly introduce metal binding capabilities or functionalization of grafted polymer chains by chelating agents. Different methodologies like photografting, high energy radiation and chemical initiation

techniques have been applied to activate the backbone or main polymer. Amide, amine, carboxyl and hydroxyl binding ligands can be employed to form free radicals followed by copolymerization and functionalization. The carboxyl functional groups play a major role in metal removal using biosorbents (Tan and Xiao, 2009). The variation in pH value can change the characterization and availability of metal ions as well as surface functional group chemistry. In lower and higher pH values ( $\text{pH} < 2$  and  $\text{pH} > 9$ ), predominant competition between hydronium cation and metal ions, and soluble hydroxyl formation are the main factors contributing to depletion of adsorption capacity (Pérez Marín et al., 2009). Recently, succinic, maleic and phthalic have been reported as good surface modification agents due to their specifications to increase carboxyl groups ( $-\text{COOH}$ ) on the surface of biosorbent. Ethylene diaminetetraacetic dianhydride (EDTAD), as a biodegradable agent with two anhydride groups per molecules, is a proper option for surface modification through occurring esterification reaction, introducing carboxylic acid and amine groups, as well as enhancing chelating abilities and biosorption capacity (Pereira et al., 2010).

Velazquez-Jimenez et al. (2013) compared different types of modifying agents for agave bagasse treatment. They reported that organic acids like citric, oxalic and tartaric acid enforced weak and ineffective functional groups which were responsible for metal adsorption. Meanwhile, the analytical results indicated that concentration of oxygenated group like carboxyl group ( $-\text{COOH}$ ) increased. This enhancement was probably obtained by modification via protonating unavailable functional groups with mineral acid like  $\text{HNO}_3$  followed by transforming and oxidizing functional groups to carboxylic groups with  $\text{NaOH}$ . In another study, according to Fourier transform infrared spectroscopy (FTIR) analysis, the number of functional acid groups such as O-H and

C–O (stretching vibrations of ethers and alcohols) increased through phosphoric acid treatment while titrable acid groups decreased through hydrogen peroxide treatment (Martín-Lara et al., 2012). Leyva-Ramos et al. (2012) also investigated the modification agent molarity to find the relationship between the capacity and acidic sites of corncob in natural and modified forms as well as the probable biosorption mechanism.

Nevertheless, it is generally difficult to compare the adsorptive properties of adsorbents directly, because there are considerable inconsistency in data presentation and differences in experimental conditions, materials and methodologies (e.g. different initial concentrations, pH value, temperature, adsorbent dose, particle size, etc).

### **3 Mechanism of biosorption process**

Biosorption process includes a combination of several mechanisms including electrostatic attraction, complexation, ion exchange, covalent binding, Van der Waals attraction, adsorption and micro-precipitation (Montazer-Rahmati et al., 2011; Witek-Krowiak, 2012). Physical adsorption takes place because of weak Van der Waals' attraction forces, whereas the so-called chemisorption is a result of relatively strong chemical bonding between adsorbates and adsorbent surface functional groups (Bhatnagar and Sillanpää, 2010).

The main mechanisms known for metal and dye adsorption on cellulosic biosorbents are chelating, ion exchanging and making complexion with functional groups and releasing  $[H_3O]^+$  into aqueous solution. Ionic exchange is known as a mechanism which involves electrostatic interaction between positive cations and the negatively charged groups in the cell walls (Fiol et al., 2006). Many studies confirmed

that ion exchange mechanism could be included in biosorption process rather than complexation with functional groups on the biosorbent surface. They also showed the role of sodium, potassium, calcium and magnesium present in the adsorbent during ion exchange (Ding et al., 2012; Tunali Akar et al., 2012; Krishnani et al., 2008).

The mechanisms also can be anticipated and verified through the understanding of the surface structure and functional groups, thermodynamic and kinetic studies as well as by combination of different methods of FTIR (Fourier Transform Infra-Red), SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-Ray), TEM (Transmission Electron Microscopy), Raman microscopy, XPS (X-ray photoelectron spectroscopy), and some conventional techniques like titration, chemical blocking of functional groups and concomitant release of cations from biosorbent during the sorption (Torab-Mostaedi et al., 2013; Witek-Krowiak, 2012; Ofomaja., 2011).

According to the results obtained from the intra-particle diffusion kinetic model, adsorption can be described as multiple sorption rates attributed to fast film diffusion, rate-limiting gradual adsorption stage (pore diffusion) and final slow equilibrium step of intra-particle transport. In batch systems, intra-particle diffusion was not the only rate controlling step but generally it is important in the biosorption kinetic process as adsorbent size was the main parameter of biosorption process (Ahmad et al. 2009). On the other hand, in continuous flow system, film diffusion is more likely the rate limiting step (Rangabhashiyam et al., 2013). The studies on Cr (VI) removal claimed that anionic chromium ion species could bind to the positively charged adsorbent surface and converted to Cr (III) through two mechanisms: 1) direct reduction by contact with the electron-donor groups of biosorbent; and 2) indirect mechanism consisting three



steps of binding of anionic chromium (IV) ion to positively-charged surface of biosorbent, reduction to Cr (III) and then release the created Cr (III) ions. Low pH values could accelerate the rate of reduction reactions in both of two mechanisms (Blázquez et al., 2009; Krishnani et al., 2008). Besides, thermodynamic study and a good perception of temperature influence on biosorption process can help to understand the adsorption mechanism (Farooq et al. 2010).

In other study, Schiewer and Patil (2008) reported that the protonated citrus peels exhibited very good ability to Pb removal very similar to some ion exchange resins. They discovered, even at high ionic strength environment, Pb removal efficiency remained more than 90% which indicated that electrostatic attraction was not the main binding mechanism.

Along with kinetic and thermodynamic studies, isotherm models can also contribute to information about mechanism of adsorption. Blázquez et al. (2010) described the types of Pb (II) biosorption on olive stone and two-phase olive mill solid. They highlighted that the type of biosorption is a function influences the shape of adsorption isotherm. This shape associates with formation of monomolecular or multimolecular layer adsorption via both strong and weak adsorbate-adsorbent interactions. Furthermore, based on hypothesis of Dubinin-Radushkevich isotherm,

mean free energy of adsorption ( $E = \frac{1}{\sqrt{2B_{D-R}}}$ ) calculated from Dubinin-Radushkevich isotherm can evaluate sorption properties and indicate if main mechanism is chemical reaction dominated by ion exchange ( $8 < E < 12$  kJ/mol) or physical adsorption ( $E < 8$  kJ/mol) (Ding et al., 2012).

#### 4 Lignocellulosic wastes and by-products for heavy metal ion removal

Lignocellulosic waste materials have proper characteristics and structural compounds to adsorb heavy metal ions on their surface binding sites through interaction with the chemical functional groups.

Without going into too much detail, the maximum biosorption capacities of different types of natural biosorbents, agro-industrial wastes and by-products for heavy metal removal are summarised in **Table 2** and some of the results are discussed hereinafter. Due to the different laboratory conditions (e.g. pH, temperature, adsorbent dose, particle size), materials and methodologies, it is not easy to conclude which biosorbent would be suitable for particular metal ion.

One of the main factors that sprightly influences whether an agro-industrial waste or by-product is practical or not is the availability. For example, sugarcane bagasse, an agro waste from sugar industries has been extensively studied because of its low price and high availability all over the world. This biosorbent exhibited very high potential in heavy metal uptake during wastewater treatment (Alomá et al., 2012; Liu et al., 2012). The biosorption capacity of sugarcane bagasse could be noticeably improved by introducing carboxylic, amine and other functional groups into the surface materials (Pereira et al., 2010) or by removing soluble organic compounds and increasing efficiency of metal sorption (Martín-Lara et al., 2010). Based on the work of Pehlivan et al. (2013), the main factors determining the adsorption of As (V) on sugarcane bagasse modified by iron (III) oxy-hydroxide (HFO) were electrostatic interactions, ligand exchange and chelation between positively charged surface groups  $\equiv\text{FeOH}^{2+}$  and negatively charged As (V) ions. Alomá et al. (2012) concluded that nickel ion

biosorption on non-chemically modified sugarcane bagasse within temperature range of 25–65°C was exothermic and spontaneous. Moreover, Langmuir isotherm was able to simulate the experimental data better than Sips and Freundlich models.

Study on optimal preparation conditions for sugarcane bagasse, watermelon rind and banana peels to use in Cu (II) removing from water was carried out by Liu et al. (2012). The results demonstrated that 120 °C was the suitable drying temperature. The drying time for sugarcane bagasse, watermelon rind and banana peel was 1, 3 and 2 h, respectively. They found that fine powder (<150µm) was the most efficient size for Cu (II) removal. However, for continuous biosorption process in column, the mechanical strength should be considered as a result of biomass particle size.

In other study, when rice husk was subjected to 1.5% alkali treatment and used for Zn (II), Cu (II), Cd (II), Ni (II), Pb (II), Mn (II), Co (II), Hg (II) and Cr (VI) removal from single ion and mixed solutions, the ultimate biosorption capacity calculated from Langmuir isotherm model was improved in the order of  $Ni^{2+} < Zn^{2+} \approx Cd^{2+} \approx Mn^{2+} \approx Co^{2+} < Cu^{2+} \approx Hg^{2+} < Pb^{2+}$  at  $32 \pm 0.5^\circ C$  between pH range of 5.5 and  $6.0 \pm 0.1$  (Krishnani et al., 2008). However, in other study, the pre-treatment of sugarcane bagasse using NaOH and HCl had no significant effect on mercury biosorption capacity (Khoramzadeh et al., 2013).

The other typical and abundantly available agro-industrial materials are wheat and barley wastes, as the main crops all over the world. The feasibility of utilization of these kinds of waste as very low-cost biosorbents were investigated by Pehlivan et al. (2012), Muhamad et al. (2010) Aydin et al. (2008). Esterified barley straw was thermo-chemically modified with citric acid for copper adsorption (Pehlivan et al., 2012).

Increasing the temperature improved the reaction efficiency but led to lower carboxyl content and increased cross-linking of modified barley straw. Increasing citric acid concentration enhanced free carboxyl groups on the biomass matrix. Besides, the results demonstrated that a significant amount of free COOH groups remained in the biomass structure up to 4 h reaction time and then the increase in cross-linking occurred with more reaction time. On the contrary, some case studies suggested the acids as modifying agent should be used in lower concentrations due to prevention of cellulose structure damage and high toxicity. In addition, Miretzky and Cirelli (2010) reported that alkali treatments in comparison with acidic ones at the same conditions were more effective on metal ion removal by solving cell wall matrix. Therefore, alkali treatments could result in better diffusion through wall and make the functional groups denser and thermodynamically more stable. The increase in Cd (II) and Cu (II) uptake on wheat straw with temperature raise was attributed to the increase in the available active sites on the surface of the adsorbent by the opening up of the cellulose fibres when wheat straw was soaked in a warmer solution (Muhamad et al., 2010).

Sawdust has also been widely studied as an alternative adsorbent and has shown good stabilities (Asadi et al., 2008; Bulut and Tez, 2007; Prado et al., 2010). It has been identified that phenolic, hydroxyl and carboxylic functional groups of sawdust are responsible for heavy metal uptake, as heavy metal ions could accumulate in secondary septum of wood in which the amount of lignin is very low. Palumbo et al. (2013) found that metal adsorption onto biosorbent is possibly a passive binding. They highlighted the effect of pH and natural organic matter on Zn removal. Metal uptake has been manipulated by pH stronger than the concentration of natural organic matter. Šćiban et al. (2007) investigated heavy metal biosorption capacity of sawdust during synthetic

and real cable factory wastewater treatment. Heavy metal ion adsorption was influenced by the existence of other ions and organic materials in real wastewater through three phenomena, namely, synergism, antagonism and non-interaction. This study showed that copper was better adsorbed from wastewater with multiple heavy metal ions than from wastewater containing single Cu (II) ion, whereas Cd adsorption was inhibited by other metal ions and Zn removal were unaffected. As expected, some metal ions have better affinity towards lignocellulosic biosorbents than other ions and this fact ascertains the selectivity potential of functional group. The highest amount of correlation coefficients, BET, Langmuir and Freundlich models well described experimental data of zinc, copper and cadmium removal, respectively.

Bulut and Tez (2007) released that Ni, Cd and Pb biosorption on walnut tree sawdust was favourable at higher temperatures as the values of  $\Delta G^\circ$  became more negative and positive  $\Delta H^\circ$  suggested endothermic nature of adsorption. The randomness at solid–solution interface increased by temperature grows (positive  $\Delta S^\circ$ ), leading to enhancement of adsorption at higher temperatures. This may be related to adsorption surface activation and/or pore size enlargement. Reverse trend was obtained for Pb biosorption on different types of sawdust as an exothermic process (Prado et al., 2010).

As a pectin–rich by–product of fruit juice industry, the suitable chemical treatment (e.g. mercapto–acetic acid ( $C_2H_4O_2S$ ) and carbon disulfide ( $CS_2$ )) can make orange peels more favorable for metal adsorption due to the negativity amount of zeta potential, indicating higher physical stability and surface activity (Sha et al., 2009).

Martín-Lara et al. (2012) investigated the biosorption properties and mechanical strength of the olive stone modified by  $H_2SO_4$  (1 M) for lead removal in a fixed–bed

column. The column was retained over 14 cycles of use and life factor revealed that biosorbent bed would be exhausted after 71.3 cycles. Furthermore, according to the work study mentioned above, all biosorption were found to achieve equilibrium in a very short contact time and all kinetic studies showed the applicability of pseudo-second-order kinetic model and the second-order nature of biosorption process of heavy metal ions onto raw and pre-treated biosorbents. This can be attributed to assumption of chemical adsorption rate-controlling step in biosorption process involving electron sharing or transferring between adsorbent and adsorbate (Pereira et al., 2010; Aloma et al., 2012; Bulut & Tez, 2007; Ding et al., 2012). **Table 2**

## **5 Lignocellulosic wastes and by-products for dye removal**

Major pollutants in industrial wastewaters are high concentrations of SS, COD, color, acidity and other soluble substances. Wastewater from dyeing operations is intense colored stream containing unfixed dyes along with salts and auxiliary chemicals such as emulsifying agents. Thus, the removal of color from textile industry and dyestuff manufacturing industry wastewaters represents a major environmental concern. In addition, resistance of dyes to biological degradation has made color removal from wastewaters more difficult, because most textile dyes have complex aromatic molecular structures that resist degradation (Guo and Ngo, 2012). Compared with other commercially used adsorbents such as activated carbon, inexpensive, locally available and effective materials can be used as a substitute for the removal of dyes from aqueous solution (Crini, 2006). An extensive list of biosorbents and the parameters affecting dye removal have been compiled in Table 3. **Table 3**

As the most commonly used dyes in textile and paper industries, the removal of methylene blue was conducted by Guimarães Gusmão et al. (2012) using succinylated sugarcane bagasse. The carboxylate functions in the sugarcane bagasse structure have negative charges to interact to cationic dyes and hence the functionality can be modified by succinic anhydride and sodium bicarbonate solution. After esterification, FTIR spectroscopy illustrated the presence of carboxylate group ( $-\text{COO}^-\text{Na}^+$ ) and symmetric stretching of ester groups ( $-\text{C}-\text{O}-\text{C}=\text{O}$ ) which were responsible to dye biosorption. In another similar study, adsorptive capability of sugarcane fibre to remove crystal violet was studied by parab et al. (2009). Compared to sawdust and coir pith biosorption, the results revealed a good correlation of Freundlich and Redlich–Peterson (R–P) isotherm models. The experimental data also indicated coir pith achieved the highest adsorption capacity followed by sawdust and sugarcane fibre.

Other researchers conducted batch and column experiments to simulate kinetics of methylene blue adsorption on calcium chloride, zinc chloride, magnesium chloride and sodium chloride treated beech sawdust. The Freundlich and Langmuir adsorption capacity in batch study remarkably increased by pre-treatments following the order of  $\text{NaCl} > \text{CaCl}_2 > \text{MgCl}_2 > \text{ZnCl}_2$ . In the case of column adsorption process, the adsorption capacity coefficient of the bed at different breakthrough values could be calculated by the Bed Depth Service Model developed by Bohart and Adams for all used modifying agents (Batzias and Sidiras, 2007). Han et al. (2007) conducted the similar study to investigate the effects of pH, adsorbate concentration, bed depth, flow rate and ionic strength and existed salt on methylene blue removal using rice husk in a continuous fixed-bed column system. The Thomas and Bed Depth Service Time models properly described the adsorption of methylene blue. Generally, breakthrough occurs faster at

higher flow rate and dye concentration due to more mass transfer rate, whereas breakthrough time increases significantly with the decrease in the flow rate. The presence of other metal ions such as  $\text{Na}^+$  and  $\text{Ca}^{2+}$  resulted in steeper slope and shorter breakthrough time. The effect of  $\text{CaCl}_2$  was stronger than that of  $\text{NaCl}$  at the same dye concentrations.

Acetone-treated capsicum seeds were used for reactive blue 49 uptake in batch and continuous column systems. According to FTIR spectra,  $-\text{NH}_2$ ,  $-\text{OH}$  and  $\text{C}=\text{C}$  groups participated in dye removal through chemisorption mechanism. This process well described by Langmuir model in both batch and continuous modes. In batch biosorption experiments, ionic strength increase made a slight decrease in dye removal efficiency, while there were no significant changes obtained by increasing initial dye concentration (Tunali Akar et al., 2011).

Asgher and Bhatti (2012) compared raw, immobilized and acetic acid-treated citrus waste to remove reactive blue 19 and reactive blue 49 from aqueous solution. Very excellent performance was achieved for both dyes. Acidic pH range was the optimum condition under which dye molecules bound with surface active sites of biomass ( $-\text{NH}_2$ ,  $-\text{OH}$  and  $\text{C}=\text{O}$  groups) via hydrogen ions as bridging ligands. The physio-sorption was the predominant mechanism of removing reactive blue 19 and reactive blue 49 biosorption using citrus waste. The biosorption process of both dyes adequately followed all Langmuir, Freundlich and Temkin isotherms.

Hameed (2008, 2009a, 2009b) investigated the methyl violet removal using sunflower seed hull and methylene blue removal using grass waste and spent tea leaves. The experimental data were analysed in terms of initial pH, initial dye



concentration, biosorbent dose and contact time in order to find the best kinetic and isotherm model. For all dyes, the pseudo-second order-order kinetic model was better than pseudo-first-order and intra particle diffusion models. Methylene violet uptake on sunflower seed hull followed Freundlich while Langmuir equation was found to be in good agreement with sorption data of methylene blue on grass and tea waste. The dye removal is strongly dependant on pH, biosorbent dose, initial dye concentration as well as biosorbent type according to the results of maximum dye biosorption capacities reported in literatures. In addition, the rough surface of these adsorbent provided a suitable bed for dye binding or entrapping according to SEM images.

The other study conducted by Madrakian et al. (2012) dealt with capability of magnetite nanoparticles loaded tea waste for adsorption of seven dyes (Janus green, methylene blue, thionine, crystal violet, Congo red, neutral red and reactive blue 19). In this study, cationic dyes indicated higher adsorption removal than anionic dyes. The authors suggested that the increase in intensity of some peaks (e.g. -OH, aliphatic C-H, C-O, NH<sub>2</sub> in amid bands) depicted in FTIR analysis could be attributed to the well effectiveness of magnetite nanoparticles modification as a chemical modifier. They also reported very excellent biosorption removal (up to 98%) for all tested dyes under optimum experimental conditions.

The possibility of using phosphoric acid (H<sub>3</sub>PO<sub>4</sub><sup>-</sup>) treated sugarcane bagasse to remove methyl red dye was explored by Saad et al. (2010). The efficiency of dye removal by H<sub>3</sub>PO<sub>4</sub><sup>-</sup> treated bagasse was less than activated carbon and followed by untreated bagasse. Study on the effect of pH indicated that activated carbon decolourization remained 100% for all pH values, whereas for both treated and untreated bagasse, lowest percentage of dye removal was recorded at pH of 2. Dye

adsorption was significantly increased between the pH value of 3 and 6 and then gradually decreased in the pH range of 7–10. This trend illustrated that ion exchange mode and electrostatic attraction between dye anions and negatively charged surface of biosorbent. The kinetics of methyl red adsorption followed the pseudo–first–order kinetic expression and Langmuir isotherms model fit well the experimental data.

Safa et al. (2011) concluded that carbonyl, carboxyl and amide groups of rice husk were involved in Direct Red–31 and Direct Orange–26 removal at low pH values. Besides, at basic pH range, formation of more ionic species such as hydroxyl and carboxyl showed competition with dye anions for active sites and hence biosorption decreased. They also reported different biosorbent surface behaviours could be seen by different chemical modification agents. More positively charged active sites and stronger electrostatic attraction were created by acid treatment and surface protonation. Alkali treatment led to surface functional group deprotonation and interior biosorbent surface activation, and salt treatment could produce more binding sites for dyes. Additionally, cationic surfactant created positive charge impregnation on adsorbent surface. These several modification methods increased dye removal on rice husk in the following order: glutaraldehyde < methanol < ethanol < NaOH < NH<sub>4</sub>OH < boiling < native < Triton X–100 < heat treated < cationic surfactant < MgSO<sub>4</sub> < CaCl<sub>2</sub>·H<sub>2</sub>O < NaCl < HNO<sub>3</sub> < H<sub>2</sub>SO<sub>4</sub> < HCl.

Akar et al. (2009) studied RR198 biosorption onto olive pomace in synthetic and real wastewater treatment. They found this process was spontaneous and endothermic in nature by calculating the thermodynamic parameters and well fitted by Langmuir isotherms better than both Freundlich and Dubinin-Radushkevich models. RR198 biosorption onto olive pomace was independent of ionic strength in the concentration

range of 0.01–0.15 M, whereas, it decreased in the ionic strength over 0.15 M. Besides, there was no tangible decrease in biosorption capacity of olive pomace when it was utilized for treating real wastewater containing several interfering species.

The feasibility of barley husk to remove synthetic dye, namely direct solar red BA, was explored by Haq et al. (2011). The thermodynamic study suggested that adsorption was physical and spontaneous due to the negative changes in free Gibbs energy. Similar to other biosorbents, biosorption capacity of barley husk either increased with the decrease of particle size or reduced with the increase of initial dye concentration (>100 ppm) in the aqueous solution. The latter might be attributed to the fact that interactions between dye anions became prevalent and subsequently, resulting in lessening affinity of the dye binding sites on the biosorbent. The authors also reported that existence of salts and anionic or cationic surfactants (detergents) in wastewater could lead to lowering dye removal.

## **6 Lignocellulosic wastes and by-products for organic and nutrient removal**

Recently, many attempts have been made for finding low-cost and effective anion/cation exchangers produced from agricultural by-products to remove organic pollutants and nutrients from aqueous solutions (Table 4). It is well known as the pH of the solution is one of the effective parameters on adsorptive potential of biomass and affects its surface charge as well as the degree of ionization of different pollutants (Ahmad et al., 2009). At higher pH, negatively charged adsorbent sites increase, which enhance the adsorption of positively charged cations through electrostatic forces of attraction. **Table 4**

Ofomaja (2011) studied the kinetics, isotherm models and possible mechanism of biosorption process in terms of removing large organic pollutant molecule like 4-nitrophenol using *Mansonia altissima* wood sawdust. From calculated kinetic rates of pollutant sorption into macro-, meso- and micropores, the process mechanism was found to be complex, consisting of both external mass transfer and intra-particle diffusion. This process was quite well described by the pseudo second-order kinetic model and Freundlich isotherm.

Brandão et al. (2010) reported that natural sugarcane bagasse could adsorb up to 99% of gasoline and 90% of n-heptane in aqueous solutions within only 5 min. However, at low concentration of gasoline and n-heptane, monolayer biosorption could be simulated by Langmuir model. However, none of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models could well describe the process at high concentration of n-heptane and for gasoline contaminated solution at concentration more than 0.04 mg/L. According to measured correlation coefficients, Freundlich presented the best simulations, followed by Dubinin-Radushkevich and Temkin isotherms and then Langmuir. The presence of ethanol in gasoline could enhance the solubility of gasoline in water, thereby improving the adsorptive capacity of sugarcane bagasse.

Achak et al. (2009) found that banana peel was a low-cost and efficient adsorbent for olive mill wastewater purification containing phenolic compounds with a high biosorptive capacity of 688.9 mg/g. Equilibrium state was attained within 3 h and 96% of phenolic compounds were removed completely. Alkali condition was more favorable for phenol adsorption and lower pH value was more suitable for desorption process. They also explained that in case of using water for biosorbent recovery, if the cation or

anion attached on biomass surface were very weak, physiosorption via Van der Waals attraction was the main mechanism. If alkali water (pH 12) was used, adsorption mechanism could be ion exchange, while chemisorption was dominant mechanism if acetic acid was employed. Based on the results, since 0.17, 0.30 and 0.12 g/g of desorbed phenolic compounds could be obtained by neutral pH water (pH 7.3), acetic acid (pH 1.2) and alkaline water (pH 12), respectively, chemisorption might be the main mechanism of phenol removal.

Maximum biosorption capacity of  $\text{NH}_4^+$  was obtained at pH of 8 using sawdust as biosorbent (Wahab et al., 2010). The biosorption was resulted from ammonium cation binding to negatively charged lignin and cellulose chains. Nevertheless, at range of acidic pH values, biosorption took place due to polar functional groups of lignin such as alcohols, aldehydes, ketones, acids and hydroxides. Equilibrium states were quickly reached within 20 min. The FTIR spectral characteristics of raw sawdust before and after ammonium biosorption illustrated that acidic groups of carboxyl and hydroxyl were predominant contributors in the complexation of ammonium ions and ion exchange processes.

Xu et al. (2010) applied a new method for preparation of wheat straw as an anion exchanger based on aminated intermediate (epoxypropyl triethylammonium chloride). Methanol solution was used as organic solvent to facilitate epichlorohydrin and triethylamine reaction, and pyridine was applied as a weak-base catalyst to open the strained epoxide rings. The maximum sorption capacities of modified wheat straw for nitrate and phosphate were approximately 52.8 and 45.7 mg/g, respectively, which could be comparable with the maximum biosorption capacity obtained from commercial anion exchange resin, activated carbon and other modified adsorbents. In addition, after

four subsequent cycles of adsorption–desorption, both of eluting agents (HCl and NaCl) showed an excellent recovery performance without significant loss in biosorption capacity.

## 7 Future perspectives

Although lignocellulosic wastes and by-products have adsorption capacity limitation in comparison with current commercial adsorbents, a good adsorbent selection with proper chemical modification can considerably improve adsorptive properties of the material. Furthermore, a suitable regeneration process of pollutant-loaded adsorbent can reduce the costs of water and wastewater treatment as well. The number of papers on batch biosorption and the current developed kinetic and isotherm models can provide proper explanation and simulation for most of the mechanism studies on biosorption process and continuous process in fixed-bed column or Continuous Stirred-Tank Reactor (CSTR).

Although many attempts have been made on heavy metal removal, but for industrial dye, organic pollutants, as well as phosphate and nitrate discharged from agricultural and industrial areas, more researches are needed. Moreover, the feasibility of using lignocellulosic wastes and by-products will be studied in pilot scale and then subsequently checked in commercial industrial scale. Besides, the disposal of used adsorbent in safe and environmental friendly way and making the valuable end-use of these wastes should be deliberately considered in future studies.

In addition, most of the investigations have been carried out to utilize a single adsorbent to remove metallic or other pollutants. However, as each kind of

lignocellulosic material has special functional groups and character, several types of appropriate biosorbents can be combined for gaining better detoxification efficiency.

## 8 Conclusions

Most recent studies on lignocellulosic agro-industrial wastes and by-products as abundant and low-cost adsorbents for water treatment and wastewater remediation have been reviewed. It can be concluded that the obtained maximum adsorption capacity, selectivity and regeneration efficiency of these materials provide some idea for selecting proper adsorbent for metallic, dye, organic pollutants and nutrient removal.

Additionally, the research can help to propose optimum operation conditions for future studies on water and wastewater detoxification, as well as to improve environmental issues of solid and aquatic industrial waste disposal.

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**Table Captions**

Table 1 Chemical composition of some common lignocellulosic materials

Table 2 The performance of different types of agro-industrial wastes for heavy metal ion removal from aqueous solutions

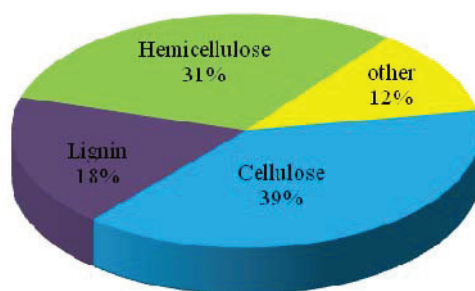
Table 3 The performance of different types of agro-industrial wastes for dye removal from aqueous solutions

Table 4 The performance of different types of agro-industrial wastes for organic and nutrient removal from aqueous solutions

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**Table 1** Chemical composition of some common lignocellulosic materials

Type	Chemical Component (%)				
	Cellulose	Lignin	Hemicellulose	Ash	Silica
Rice straw	25-35	10-15	20-30	15-20	9-15
Wheat straw	30-35	16-21	26-32	4.5-9	3-7
Barley straw	30-35	14-15	24-29	5-7	3-6
Sugarcane bagasse	32-44	19-24	25-35	1.5-5	<4
Bamboo	26-43	21-31	15-26	1.7-5	<1
Grass	30-40	10-25	35-50	5-15	-
Corn cob	35-45	5-15	35-45	1-2	<1
Leaves	15-25	5-10	70-80	<1	-
Cotton waste	80-95	-	5-20	<1	-
Hardwood	40-55	20-25	25-40	<1	-
Softwood	40-50	25-35	25-35	<1	-
Olive stone	30-35	20-25	20-30	<1	5-9
Nut shell and stone	25-35	30-40	25-30	-	-



**Table 2** The performance of different types of agro-industrial wastes for heavy metal ion removal from aqueous solutions

Adsorbent (modifying agent)	Adsorbate	$q_{\max}$ (mg/g)	Mechanism	Reference
Agave Bagasse (raw)	Cd	13.27	Ion exchange, complexation	Velazquez-Jimenez et al., 2013
Agave Bagasse (HCl)	Cd	13.5	Ion exchange, complexation	Velazquez-Jimenez et al., 2013
Agave Bagasse (HNO <sub>3</sub> )	Cd	12.5	Ion exchange, complexation	Velazquez-Jimenez et al., 2013
Agave Bagasse (NaOH)	Cd	18.32	Ion exchange, complexation	Velazquez-Jimenez et al., 2013
Rice straw (raw)	Cd	13.89	Ion exchange, chelating	Ding et al., 2012
Grapefruit peel (raw)	Cd	42.09	Ion exchange	Torab-Mostaedi et al., 2013
Corn cob (Citric acid)	Cd	49.2	Ion exchange	Leyva-Ramos et al., 2012
Wheat stem (raw)	Cd	11.6	Complexation	Tan and Xiao, 2009
Wheat stem (Methanol)	Cd	0.35	Complexation	Tan and Xiao, 2009
Wheat stem (NaOH)	Cd	21.84	Complexation	Tan and Xiao, 2009
Coconut shell <sup>(a)</sup> (raw)	Cd	37.78		Sousa et al., 2010
Coconut shell <sup>(b)</sup> (raw)	Cd	11.96		Sousa et al., 2010
Rice husk (raw)	Cr	8.5	Complexation, ion exchange and surface precipitations	Bansal et al., 2009
Rice husk (Formaldehyde)	Cr	10.4	Complexation, ion exchange and surface precipitations	Bansal et al., 2009
Rice husk (Alkali-treated)	Cr	52.1	Ion exchange	Krishnani et al., 2008
Olive pomace (raw)	Cr	13.95	Ion exchange	Krishnani et al., 2008
Orange peel (raw)	Cu	50.94	Ion exchange, complexation	Sha et al., 2009
Orange peel (C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> S)	Cu	70.67		
Sunflower hull (raw)	Cu	57.14		Witek-Krowiak, 2012
Barley straw (raw)	Cu	4.64	Ion exchange, chelation	Pehlivan et al., 2012
Barley straw (Citric acid)	Cu	31.71	Ion exchange, chelation	Pehlivan et al., 2012
Garden grass (raw)	Cu	58.34		Hossain et al., 2012
Coconut shell (raw)	Cu	41.36		Sousa et al., 2010
Lentil shell (raw)	Cu	9.59		Aydin et al., 2008
Rice shell (raw)	Cu	2.95		Aydin et al., 2008
Wheat shell (raw)	Cu	17.42		Aydin et al., 2008
Sawdust (raw)	Cu	6.88		Šćiban et al., 2007
Rice straw (HNO <sub>3</sub> -NaOH)	Cu	8.13		Rocha et al., 2009
Olive stone (raw)	Cu	20.2		Fiol et al., 2006
Coconut shell <sup>(a)</sup> (raw)	Cu	41.36		Sousa et al., 2010
Coconut shell <sup>(b)</sup> (raw)	Cu	20.26		Sousa et al., 2010
Agave Bagasse (raw)	Pb	35.6	Ion exchange, complexation	Velazquez-Jimenez et al., 2013
Agave Bagasse (HCl)	Pb	54.29	Ion exchange, complexation	Velazquez-Jimenez et al., 2013
Agave Bagasse (HNO <sub>3</sub> )	Pb	42.31	Ion exchange, complexation	Velazquez-Jimenez et al., 2013
Agave Bagasse (NaOH)	Pb	50.12	Ion exchange,	Velazquez-Jimenez et

Adsorbent (modifying agent)	Adsorbate	$q_{\max}$ (mg/g)	Mechanism	Reference
Rice husk (Alkali-treated)	Pb	58.1	complexation	al., 2013
Corncob (raw)	Pb	16.22	Ion exchange	Krishnani et al., 2008
Corncob (CH <sub>3</sub> OH)	Pb	43.4		Tan et al., 2010
Corncob (NaOH)	Pb	7.89		Tan et al., 2010
Sawdust (raw)	Pb	15.9	Ion exchange, complexation	Bulut and Tez, 2007
Olive stone (raw)	Pb	92.6		Fiol et al., 2006
Coconut shell <sup>(a)</sup> (raw)	Pb	54.62		Sousa et al., 2010
Coconut shell <sup>(b)</sup> (raw)	Pb	17.9		Sousa et al., 2010
Agave Bagasse (raw)		2.23		Alomá et al., 2012
Sawdust (raw)	Ni	3.29	Ion exchange, complexation	Bulut and Tez, 2007
Rice husk (Alkali-treated)	Ni	5.52	Ion exchange	Krishnani et al., 2008
Grapefruit peel (raw)	Ni	46.13	Ion exchange	Torab-Mostaedi et al., 2013
Cashew nut shell (raw)	Ni	18.86		Kumar et al., 2011
Olive stone (raw)	Ni	21.3		Fiol et al., 2006
Coconut shell <sup>(a)</sup> (raw)	Ni	16.34		Sousa et al., 2010
Coconut shell <sup>(b)</sup> (raw)	Ni	3.12		Sousa et al., 2010
Agave Bagasse (raw)	Zn	7.84	Ion exchange, complexation	Velazquez-Jimenez et al., 2013
Agave Bagasse (HCl)	Zn	14.43	Ion exchange, complexation	Velazquez-Jimenez et al., 2013
Agave Bagasse (HNO <sub>3</sub> )	Zn	12.4	Ion exchange, complexation	Velazquez-Jimenez et al., 2013
Agave Bagasse (NaOH)	Zn	20.24	Ion exchange, complexation	Velazquez-Jimenez et al., 2013
Agave Bagasse (EDTAD) <sup>(c)</sup>	Zn	105.26	Ion exchange	Pereira et al., 2010
Agave Bagasse (EDTAD) <sup>(d)</sup>	Zn	45.45		Pereira et al., 2010
Sawdust (EDTAD) <sup>(c)</sup>	Zn	80	Ion exchange	Pereira et al., 2010
Sawdust (EDTAD) <sup>(d)</sup>	Zn	47.39		Pereira et al., 2010
Sawdust (raw)	Zn	0.96		Šćiban et al., 2007
Rice straw (HNO <sub>3</sub> -NaOH)	Zn	8.63		Rocha et al., 2009
Rice husk (Alkali-treated)	Zn	8.14	Ion exchange	Krishnani et al., 2008
Coconut shell <sup>(a)</sup>	Zn	17.08		Sousa et al., 2010
Coconut shell <sup>(b)</sup>	Zn	7.32		Sousa et al., 2010
Rice straw (raw)	Hg	22.06		Rocha et al., 2009
Rice husk (raw)	Hg	36.1		Krishnani et al., 2008
Sugarcane Bagasse (raw)	Hg	35.71		Khoramzadeh et al., 2013

<sup>(a)</sup> single-component solution

<sup>(b)</sup> multi-component solution

<sup>(c)</sup> Synthetic wastewater

<sup>(d)</sup> Real wastewater

**Table 3** The performance of different types of agro-industrial wastes for dye removal from aqueous solutions

Adsorbent	Modifying agent	Adsorbate	$q_{\max}$ (mg/g)	Reference	
Sugarcane Bagasse	Succinic anhydride	Methylene blue	478.5	GuimarãesGusmão et al., 2012	
		Gentian violet	1273.2	GuimarãesGusmão et al., 2012	
Sugarcane Bagasse	raw	Crystal violet	10.44	Parab et al., 2009	
Sugarcane Bagasse	raw $H_3PO_4$	Methyl red	5.66	Saad et al., 2010	
		Methyl red	10.98	Saad et al., 2010	
Jute fibre	raw	Congo red	8.116	Roy et al., 2013	
Rice husk	raw	Direct red–31	74.07	Safa et al., 2011	
	Carboxymethyl cellulose sodium	Direct red–31	41.84	Safa et al., 2011	
	Polyvinyl alcohol+sodium alginate	Direct red–31	11.44	Safa et al., 2011	
	HCl	Direct red–31	74.63	Safa et al., 2011	
	raw	Direct orange–26	53.19	Safa et al., 2011	
	Carboxymethyl cellulose sodium	Direct orange	34.25	Safa et al., 2011	
	Polyvinyl alcohol+sodium alginate	Direct orange	16.78	Safa et al., 2011	
	HCl	Direct orange	46.95	Safa et al., 2011	
	Barley husk	raw	Solar red BA	400	Haq et al., 2011
	Citrus waste	raw	Reactive blue 19	37.45	Asgher and Bhatti, 2012
Sodium alginate immobilized		Reactive blue 19	400	Asgher and Bhatti, 2012	
Glacial acetic acid		Reactive blue 19	75.19	Asgher and Bhatti, 2012	
raw		Reactive blue 49	135.16	Asgher and Bhatti, 2012	
Sodium alginate immobilized		Reactive blue 49	80.00	Asgher and Bhatti, 2012	
Glacial acetic acid		Reactive blue 49	232.56	Asgher and Bhatti, 2012	
Acetone		Reactive blue 49	96.35	Tunali Akar et al., 2011	
<i>Capsicum annuum</i> seed	raw	Basic Red 18	172.41	Mavioglu Ayan et al., 2012	
	$HNO_3$	Basic Red 18	272.92	Mavioglu Ayan et al., 2012	
	$H_3PO_4$	Basic Red 18	280.73	Mavioglu Ayan et al., 2012	
	raw	Methylene blue	94.34	Mavioglu Ayan et al., 2012	
	$HNO_3$	Methylene blue	142.86	Mavioglu Ayan et al., 2012	

Adsorbent	Modifying agent	Adsorbate	$q_{\max}$ (mg/g)	Reference
	H <sub>3</sub> PO <sub>4</sub>	Methylene blue	147.06	Mavioglu Ayan et al., 2012
	raw	Acid Red 111	50.0	Mavioglu Ayan et al., 2012
	HNO <sub>3</sub>	Acid Red 111	112.36	Mavioglu Ayan et al., 2012
	H <sub>3</sub> PO <sub>4</sub>	Acid Red 111	39.84	Mavioglu Ayan et al., 2012
Date stone	raw	Methylene blue	43.47	Belala et al., 2011
Palm tree waste	raw	Methylene blue	39.47	2011
<i>Artocarpusheterophyllus</i> (jackfruit) leaf powder	raw	Crystal violet	43.39	Saha et al., 2012
Sunflower seed hull	raw	Methylene violet	92.59	Hameed, 2008
Grass waste	raw	Methylene blue	457.64	Hameed, 2009a
Spent tea leaves	raw	Methylene blue	300.05	Hameed, 2009b
Olive pomace	raw	RR198	$7.21 \times 10^{-5}$ <sup>(a)</sup>	Akar et al., 2009
	raw	RR198	41.38	Akar et al., 2009
Beech sawdust	Calcium chloride	Methylene blue	12.2±1.8	Batzias and Sidiras, 2007
	Zinc chloride		13.2±2.0	Batzias and Sidiras, 2007
	Magnesium chloride		15.6±2.4	Batzias and Sidiras, 2007
	Sodium chloride		9.7±0.6	Batzias and Sidiras, 2007
Mango seed	raw	Victazol Orange	44.8	Alencar et al., 2012
	HCl		71.6	Alencar et al., 2012
Tea waste	FeCl <sub>3</sub> .6H <sub>2</sub> O+FeCl <sub>2</sub> .4H <sub>2</sub> O	Janus green	129.87	Madrakian et al., 2012
		Methylene blue	119.05	Madrakian et al., 2012
		Thionine	128.21	Madrakian et al., 2012
		Crystal violet	113.64	Madrakian et al., 2012
		Congo red	82.64	Madrakian et al., 2012
		Neutral red	126.58	Madrakian et al., 2012
		Reactive blue 19	87.72	Madrakian et al., 2012

<sup>(a)</sup> mol/g



**Table 4** The performance of different types of agro-industrial wastes for organic and nutrient removal from aqueous solutions

Adsorbent	Modifying agent	Adsorbate	$q_{\max}$ (mg/g)	Reference
Sugarcane Bagasse	raw	Gasoline	8.36	Brandoa et al., 2010
		n-heptane	2.77	Brandoa et al., 2010
Sawdust	raw	Ammonium	1.7	Wahab et al., 2010
Sawdust	raw	4-nitrophenol	21.28	Ofomaja, 2011
Wheat straw	raw	Nitrate	0.14 $\otimes$ 10 <sup>-3(a)</sup>	Wang et al., 2007
	Epichlorohydrin	Nitrate	2.08 $\otimes$ 10 <sup>-3(a)</sup>	Wang et al., 2007
Wheat straw	Epichlorohydrin	Nitrate	52.8 $\pm$ 1.0	Xu et al., 2010
		Phosphate	45.7 $\pm$ 1.1	Xu et al., 2010
Wheat stalk	Epichlorohydrin	Phosphate	60.61	Xu et al., 2011
Cotton stalk	Epichlorohydrin	Phosphate	50.54	Xu et al., 2011
Banana peel	raw	Phenol	688.9	Achak et al., 2009

<sup>(a)</sup> mol/g

**Highlights**

- This review focuses on agro-industrial wastes/by-products as low-cost biosorbent
- Current studies on heavy metal, dye, organic and nutrient biosorption are reviewed
- The effectiveness of biosorbents and their modification are discussed
- Parameters affecting the biosorptive capacity are reviewed
- Maximum biosorption capacity of different typical lignocellulosics are reported