Cactus material-based adsorbents for the removal of heavy metals and dyes: a review

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Abstract

Cactus is cultivated in many regions over the world. Because of its chemical composition and its valuable nutritional and biological characteristics, cactus finds applications in different sectors such as the pharmaceutical and the food industries. Interestingly, cactus materials (cladodes, fruit seeds, peel, etc.) have been explored for their probable use as adsorbents for the removal of toxic heavy metals and dyes from wastewater. Various preparations methods were used to produce cactus material-based biosorbents. These biosorbents have been investigated and successfully used for the elimination of both heavy metal and dyes from aqueous solutions. Related results showed very promising pollutant removal efficiency associated with an interesting adsorption capacity similar to other materials from various origins. This paper explores various cactus biosorbents preparations. Furthermore, their efficiency in depollution and factors controlling the adsorption capacity will be discussed.

1. Introduction

Water pollution is an increasing environmental problem associated mainly to industrial development. For their processes, industries utilize large quantity of water generating contaminated effluents. Because freshwater resources are limited, the use of treated wastewater for industrial processing is gradually becoming a familiar practice worldwide (Vishali and Karthikeyan, 2015). The reuse of wastewater through the employment of various treatment methods is beneficial to resolve water shortage, to preserve the high-quality resources for potable use only and to decrease pollution of surface waters. Heavy metals and dyes are two examples of the largely widespread pollutants in industrial effluents that may have severe problems for the environment including the human health (Jaishankar et al 2014, Tchounwou et al 2012). Decontamination processes involved physical, biological and chemical techniques. The available technologies are classified into conventional methods (particularly activated sludge, coagulation-flocculation, chemical precipitation, adsorption and filtration), established recovery methods (ion exchange, oxidation, solvent extraction, electrochemical treatments, membrane bioreactors, etc) and emerging methods (advanced oxidation, biosorption, adsorption into non-conventional materials, nanofiltration, etc) (Crini and Lichtfouse 2019). Because of diverse factors related to economical and technological considerations, limit number of wastewater treatment processes is universally used by various industries to treat their effluents. Interestingly, the adsorption, which is considered as safe, clean, efficient and technical feasible process, is frequently employed to remove various pollutants such as heavy metals and dyes. Therefore, the adsorption method is an interesting separation technique using suitable material called absorbent characterized by high surface area and porosity and allowing rapid adsorption equilibrium kinetics (Crini and Badot 2010, Amari et al 2018). Various factors (high efficiency, ecofriendly, low cost, capacity to remove different inorganic and organic pollutants, absorbent material resistance to toxic
substances, high effectiveness, simple design and easy operation) make this technology the most widespread method for water depollution (Farooq et al 2010, Salleh et al 2011, Bazrafshan et al 2016).

The adsorption is a procedure based on pollutant transfer from aqueous solution to the adsorbent (Crini and Badot 2010). Using experimental data, equilibrium modelling, kinetics and thermodynamic factors should be studied to determine the suitability and the applicability of an adsorbent in removing pollutant (Douven et al 2015, Allen et al 2004). Generally, data of the equilibrium adsorption were analyzed using mainly the Langmuir, Freundlich, Temkin, Dubinin-Radushkevik and the Halsey isotherm models. However, kinetics results were described commonly via pseudo first order, pseudo second order, Elovich equation and intra particle diffusion models (Malkoc and Nuhoglu 2007, Mahamadi and Nharingo 2010, Nharingo and Hunga 2013, Nharingo et al 2013). Activated carbon is mostly applied as adsorbent for pollutants removal from wastewater (Agrawal et al 2017). Nevertheless, carbon adsorption is very expensive and the process cost is related to the used material and its regeneration after exhausting (Li et al 2015). The loss of adsorption efficiency after regeneration, may limit its use. Consequently, the substitution of activated carbons with other useful material was studied by many investigators. Excellent alternative material of activated carbon should be available, inexpensive and chemically regenerable with efficient quantitative recovery. In this perspective, various green adsorbents materials were investigated (Kyzas and Kostoglou 2014, Mahfoudhi and Boufi 2017). These new materials included natural materials, agricultural by-products and industrial wastes (Ali and Gupta 2006, Bhatnagar and Sillanpaa 2010, Sharma et al., Abdolalia et al 2014). Among the studied materials, cactus based materials reached large consideration in water treatment due to its abundance accessibility, biodegradability and safe behaviour. In this context, it was reported its successful use and its efficient removal rate of various pollutants (dyes, pesticides, turbidity, carbon, heavy metals, etc) by treated or untreated cactus materials.

This paper will review the use of cactuses and their modified materials as adsorbents for the removal of toxic heavy metals and dyes.

2. Cactuses: origin and characteristics

Cactus is a member of the plant family Cactaceae originated from arid and semi-arid zones. The Cactaceae family consists of large number of genera and species, which were found in many regions over the world (South America, North Africa, Australia, Asia, etc) (De Leo et al 2010, Matthaus and Ozcan 2011, Finti et al 2013, Abdel-Hameed et al 2014, Betatache et al 2014, Osuna-martinez et al 2014, Saravanakumar et al 2015). Cactus parts mainly, cladodes, fruits, and flowers of different species have been well studied and characterized.

Table 1 summarized the proximate composition protein, lipid, ash and carbohydrates), the major minerals and fatty acids content of cactus samples collected from various regions. Generally, cactus contains protein and lipid at low concentrations, however carbohydrates represent the major component for all samples (percentage on dry weight base ranged between 40 and 93%). According to Hernandez-Urbiola et al (2011), this amount increased with cactus age. Besides, cactus is a good source of minerals mainly Ca, K, Mg, Mn and Na which represent the major minerals. Concerning the lipid content, palmitic (C16:0), linoleic, linolenic and oleic were the main fatty acids recorded in samples. In addition to data presented in table 1, it was demonstrated by many researchers that cactus species contain various bioactive molecules with interesting nutritional and biological properties (antimicrobial, antioxidant, etc) valuable in different sectors (food industry, pharmaceutical industry, etc) (Ammar et al 2012, Sharif et al 2013, El-Mostafa et al 2014, Ammar et al 2015, Silva-Hughes et al 2015, Slimen et al 2016, Ondarra 2016, Tilahun, Welegerima (2018)). Moreover, other chemicals (phenolics, carotenoids, flavonoids, flavonols, ascorbic acid, betalains, vitamins, terpenes, etc) were evaluated in cactus samples (Saravanakumar et al 2015, El-Mostafa et al 2014, Jimenez-Aguilar et al 2014), Nadia et al 2013, Khatabi et al 2013, Hernandez-Urbiola et al 2010).

The data reported by the literature showed slight variation of cactus chemical composition depending on diverse factors (sample handling and preparation, species, location, age, etc). Because of their chemical compositions, cactuses were used mainly in food for humans and forage for animals. Moreover, cactus could be used for wastewater treatment processes including the coagulant/flocculant, the adsorption, the biofiltration, sludge conditioning, etc (Ben Rebah and Siddeeg 2017).

3. Heavy metal removal

The majority of heavy metals are poisonous or carcinogenic even at low concentrations. Their presence represents an important environmental health problem. Exposition to heavy metals attacks the function of the central nervous and damages the blood content and many other organs such as lungs, liver, etc. Moreover, exposure may cause other health problems such as muscular and neurological degeneration (Jaishankar et al 2014, Tchounwou et al 2012) Consequently, the elimination of metals, mainly from aqueous solutions via
Table 1. Chemical characteristics of cactus materials collected from various locations.

| Cactus materials/species/location                  | Proximate composition (%w/w) | Major minerals (mg/100 g) | Major fatty acid (%w/w) | References                  |
|---------------------------------------------------|-----------------------------|---------------------------|--------------------------|-----------------------------|
| Cladodes *O. ficus-indica* (L.) (Central Kenya)   | 1.03% P; 0.4% L; 4.03% A and 92.57% C | Ca: 316.5; K: 108.8 Mg: 63.4; Mn: 37.8 Na: 18.7 | nd                       | Chiteva and Wairagu 2013    |
| Cladodes (dried at 60 °C) *O. ficus indica* (Mexico) | 52% P; 2.3% L; 20.46% A and 68.09% C | nd                       | Palmitic: 26.83% Linoleic: 28.61% Linolenic: 21.58% lecic: 11.03% | Lopez-Cervantes et al 2011 |
| Cladodes *O. sulphurea* (Argentina)               | 3.8% P; 0.8% L; 19.5% A and 42.5% C | nd                       | Linoleic: 25.58% Linolenic: 27.41% Oleic: 11.4% | Carreira et al 2014         |
| Cladodes *O. ficus indica* (Mexico)               | 7.44%–6.77% P; 1.79%–2.27% L; 18.58%–23.28% A and 45.21%–58.22% C | Ca: 1795–3440; K: 5520–6335 Mg: 8–29 Mn: 880–955 Na: 20–55 | nd                       | Hernandez-Urbiola et al 2011 |
| Cladodes *O. streptacantha* (Mexico)              | 11.2% P; 0.73% L; 12.6% A and 75.47% C | nd                       | nd                       | Astello-Garcia et al 2015    |
| Cladodes *O. hyptiacantha* (Mexico)               | 11% P; 0.8% L; 15.1% A and 73.1% C | nd                       | nd                       | Astello-Garcia et al 2015    |
| Cladodes *O. megalacantha* (Mexico)               | 10.7% P; 0.69% L; 13.6% A and 75.01% C | nd                       | nd                       | Astello-Garcia et al 2015    |
| Cladodes *O. ficus-indica* (Algeria)              | 1.72% P; 0.14% L; 23.45% A and 74.69% C | nd                       | nd                       | Abdessemed et al 2014        |
| Cladodes *O. ficus-indica* (Mexico)               | 11.2% P; 0.69% L; 14.4% A and 73.71% C | nd                       | nd                       | Astello-Garcia et al 2015    |
| Cladodes *O. ficus-indica* (Egypt)                | 7.78% P; 2.36% L; 28.96% A and 60.9% C | Ca: 627; K: 2430 Mn: 13.8; Na: 63 | nd                       | El-safy 2013                |
| Cladodes *O. albicarpa* (Mexico)                  | 11.6% P; 0.75% L; 13.2% A and 74.45% C | Ca: 647; K: 1957 Mn: 24.1; Na: 77 | nd                       | Astello-Garcia et al 2015    |
| Cladodes *O. ficus indicar Inermis* (Tunisia)      | 6.9% P; 4.9% L; 21.4% A and 66.8% C | Mg: 78.7; Ca: 44.2 Zn: 15.2 | nd                       | Bakari et al 2017           |
| Mucilage *O. stricta* (Ethiopia)                  | 5.86% P; 0.43% L; 33.9% A and 59.81% C | nd                       | nd                       | Gebresamuel and Gebre-Mariam 2012 |
| Mucilage *O. ficus-indica* (Mexico)               | 8.74% P; 3.95% L; 25.65% A and 60.36% C | nd                       | nd                       | Torres et al 2014           |
| Mucilage *O. ficus-indica* (Ethiopia)             | 7.71% P; 0.47% L; 38.43% A and 53.39% C | nd                       | nd                       | Gebresamuel and Gebre-Mariam 2012 |
| Mucilage *O. ficus-indica* (Mexico)               | Protein: 1.18% P; 2.62% L; 22.93% A and 73.25% C | Ca: 310                  | nd                       | Espino-Díaz et al (2010)    |
| Fruits *O. joconostle* (Mexico)                   | 0.71%–1.56% P; *0.1% L; 0.49%–0.65% A and 5.81%–7.98% C | Nd                      | nd                       | Contreras et al 2011        |
| Flowers: *O. ficus-indica f. inermis* (Tunisia)    | 8%–16.9% P; 1.2%–3.5% L; 1.2%–7.2% A and 72.7%–89.6% C | Ca: 399–655; K: 1612–1945 Mg: 286–381 Na: 73–126 Fe: 6.3–14 | nd                       | Ennouri et al 2014          |

P: protein; L: lipid; A: ash; C: carbohydrate; nd: not determined.
Table 2. Examples of cactus material-based biosorbents for heavy metal removal from aqueous solutions.

| Cactus material-based biosorbent preparation | Removal efficiency (Y in %)/biosorption capacity (Q in mg/g) /conditions/isotherm | References |
|---------------------------------------------|---------------------------------------------------------------------------------|------------|
| Water extraction of cactus polyelectrolyte with water (132 g in 750 ml water, stirred for 30 min). | Y : 38.50% for Cu (II) | Gad et al 2010 |
| | Y : 16.12% for Cd (II) | |
| | Y: 30.12% for Fe (III) (dosage 10% (v/v), 150 rpm, 30°C) | |
| | Q: 30.42 mg l⁻¹ for Cd (II) (dosage 2 g l⁻¹, pH 5.8 and 25°C) | Barka et al 2013a |
| O. ficus-indica cactus (cladodes): Sundried (3 weeks), cutted into small pieces, dried (60 °C, 24 h) and powdered (*100 μm) | Q: 98.62 mg g⁻¹ for Pb(II) (dosage of 2 g l⁻¹, pH 3.5 and 25°C) | |
| | Q: 19.68 mg g⁻¹ for Cr(VI); Langmuir | |
| Ficus carica bast fiber | Q: 3.5 mol kg⁻¹ for Cu (II) (dosage 6.7 g l⁻¹, pH 6.5, 25°C and 24 h reaction time,); Langmuir | Gupta et al 2013 |
| Activated biochar prepared from O. ficus indica catus fibres (cladodes): sundried, disintegrated, washed, dehydrated (70 °C), carbonization (200 °C, 30 min and 600 °C, 1 h), activated with HNO₃ (12 M at room temperature and 5 h at 80 °C), washed with water, neutralized, dried (100 °C), ground and sieved (200–500 μm) | Q: 0.65 mol kg⁻¹ for Cu (II) | Hadjittos et al 2014 |
| | Phosphorylated cactus fiber | |
| | Q: 0.30 mol kg⁻¹ for Cu (II) | |
| | MnO₂-coated cactus fiber | |
| | Q: 1.56 mol kg⁻¹ for Cu (II) (dosage 6.7 g l⁻¹, pH 6.5, 23 °C and 24 h reaction time,), Langmuir | |
| | Non treated cactus fiber: | Prodromou and Pashalidis 2013 |
| Cactus (cladodes): washed with water, cutted in to small pieces, epidermis removed, gel dried (80–90 °C) and ground into powder | Y: 65% for Pb and Cd (dose : 1 g l⁻¹, 2 °C in the presence of 1 g/l NaCl), Frunkin isotherm | Derbe et al 2015 |
| O. ficus-indica cactus mucilage biocomposite (non-gelling extract): cactus mucilage (0.5–2 mg/l) mixed with sodium alginate (3%–5%) and added to CaCl₂ solution (0.5–1 mg/l). The liquid extract filtered, precipitated (acetone), washed (ethanol-water), dried and pulverized with ceramic mortar | Y: 59.8% and Q: 97.1 mg/g for As(V) (formulation with 1.25 mg l⁻¹ gelling mucilage, 4% sodium alginate and 0.75 mol l⁻¹ CaCl₂) | Vecino et al 2016 |
| O. ficus-indica cactus mucilage biocomposite (gelling extract): cactus mucilage (0.5–2 mg/l) mixed with sodium alginate (3%–5%) and added to CaCl₂ solution (0.5–1 mg/l). Extract precipitated (acetone and sodium hexametaphosphate/NaOH), stirred, filtered, adjustment to pH 2 of the filtrate pH adjusted (pH 2 with HCl), precipitated (HCl, 5 °C), centrifuged, residue pH adjusted (pH 8 with NaOH), filtrated (1.2 μm 0.45 μm membrane), re-precipitated (acetone), washed, dried and pulverized with a ceramic mortar | Y: 63% and Q: 101.6 mg/g for As(V) (formulation with 1.25 mg l⁻¹ gelling mucilage, 4% sodium alginate and 0.75 mol l⁻¹ CaCl₂) | Vecino et al 2016 |
| O. ficus-indica cactus mucilage (gelling extract): cactus cutted, heated (20 min, 80–85 °C, 1% NaCl), blended, neutralized (NaOH, 1 M), centrifuged (4000 rpm, 10 min), the residue used for the extraction. | Q: 2.8–0.14 mg/g for As(V) | Fox et al 2012 |
| Ectodermis of cactus fruits: washed, su-dried (7days), dehydrated (343 K, 24 h), crushed, milled, sieved, treated with formaldehyde (0.2%) or HCl (10–4 M) and redried (343 K). | Q: 30.1 mg g⁻¹ (with formaldehyde) and Q: 15.2 mg g⁻¹ (with HCl) for Cr(VI), Langmuir | Lopez-Gonzalez et al (2012) |
| Cactus peel: washed with water, air-dried (4–6 days), powdered and sieved (10, 15 and 20 mm) | Q: 30.1 mg g⁻¹ (with formaldehyde) and Q: 15.2 mg g⁻¹ (with HCl) for Cr(VI), Langmuir | |
| Cactus cladodes: washed with water, cutted (4 cm), dried (60 °C for 48 h), ground and sieved (1 mm), treated | Y: 36.02%, 17.1% and 22.8% for Mn (dosage 0.5 g l⁻¹ and particle size 10, 15 and 20 mm respectively) | Belayneh and Batu 2015 |
| | | Fernandez-Lopez et al 2014 |
Table 2. (Continued.)

| Cactus material-based biosorbent preparation | Removal efficiency (Y in %)/biosorption capacity (Q in mg/g)/conditions/isortherm | References |
|---------------------------------------------|---------------------------------------------------------------------------------|------------|
| with H2SO4(30 rpm, 24 h), washed with millipore water and redried at room temperature. | Y: 81% and Q: 5.1 mg/g for Cr (VI) (dose 2 g L⁻¹, pH 2 and 24 and 24 h contact time), Langmuir and Freundlich |  |
| Ectodermis of cactus fruit: washed with water, cutted (4 cm), dried (60 °C for 48 h), grounded and sieved (1 mm), treated with H2SO4 (30 rpm, 24 h), washed with millipore water and redried at room temperature. | Y: 83% and Q: 5 mg/g for Cr (VI) (dose 2 g L⁻¹, pH 2 and 24 and 24 h contact time), Langmuir and Freundlich | Fernandez-Lopez et al 2014 |
| Untreated cactus | Y: 36.0% for Zn; Y: 33.2% for Mn | Abhra et al 2019 |
| Cactus treated with NaOH | Y: 95.9% for Zn; Y: 88.6% for Mn | Abhra et al 2019 |
| Cactus treated with HCl | Y: 84.6% for Zn; Y: 71% for Mn | Abhra et al 2019 |
| Cactus fruit peel | Q: 14.03 mg/g for Cd (dosage 0.1 g L⁻¹, pH 4, T: 25 °C and 24 h contact time), Langmuir | Keshri et al 2017 |
| Cactus fruit peel: boiled in distilled water, sun-dried (20 days), washed with bidistilled water, dried (40–50 °C) and crushed (<0.315 mm) | Y: 93% and Q: 129.87 mg/g for Zn, Langmuir | Seghier et al 2017a |

Different preparations of cactus material used as biosorbent, was studied by many researchers (Table 2). Generally, results varied depend mainly on the used preparation and the operating conditions (pH, temperature, heavy metal concentrations, biosorbent dosage and size, etc.). In order to describe the adsorption equilibrium data and selecting optimum operating conditions, kinetic study is required. Generally, several models could be used to investigate the adsorption kinetics of heavy metals on cactus-based materials. The pseudo first-order kinetic model, the pseudo-second-order model, the intra-particle diffusion model and the Elovich model are the most commonly used to provide the mechanism involved in the sorption process (Louati et al 2018). These models are frequently used in several works in the same field showing a good determination coefficient (R²) sometimes close to 1 (Kumar and Barakat 2013, Fernández-López et al 2014, Sakr et al 2019). Equilibrium adsorption isotherm of pollutants such as heavy metals and dyes on cactus-based materials were analyzed using several mathematical models: Langmuir, Freundlich, Sips, Dubinin-Raduskevich, Temkin, Redlich, Peterson and BET (Abdelkarim et al 2017, Louati et al 2018, Georgin et al 2019, Abhra et al 2019). Adsorption isotherms data are important for the design of the sorption in flow systems. However, the Freundlich and Langmuir models are the most frequently used to predict the adsorption equilibrium between the liquid phase and the solid phase concentrations (Benderdouche et al 2003). As indicated in table 2, these two models were the most adopted models for heavy metal removals by cactus-based materials. The Langmuir model assumes that the adsorption occurs on a specific homogeneous surface by monolayer adsorption. It is also considering that the coverage of adsorbate is of equal energy of adsorption on the surface of adsorbent. The binding sites have equal affinity and can be either chemical or physical. The Freundlich isotherm is an empirical model that assumes adsorption occurs on a heterogeneous surface as well as multilayer adsorption (Pelaez-Cid et al 2013).

As reported in table 2, both cladodes and fruit ectodermis of O. ficus-indica cactus were evaluated as biosorbents (Fernandez-Lopez et al 2014). These materials were washed, cutted, dried (48 h at 60 °C), crushed and sieved (<18 mesh) to be used to remove Cr(VI) from aqueous solution. A higher level of biosorption (>80%) was achieved at 1 g L⁻¹ of biosorbent, pH 2 and at Cr(II) initial concentration of 2 mg/l. Fruit ectodermis and cladodes showed maximum adsorption round 5 mg g⁻¹. Similarly, dried and powdered cactus (O. ficus-indica) cladodes allowed high maximum adsorption ability of both Pb (98.62 mg g⁻¹ obtained with a dosage of 10 mg l⁻¹ and pH 3.5) and Cd (30.42 mg g⁻¹ obtained with a dosage of 4 g l⁻¹ and pH 3.5) (Barka et al 2013a). Dried cactus peels with different sizes (10–20 mm) were also tested for the removal of Mn. Interestingly, the highest removal level (36.02%) was obtained with 0.5 g of 10 mm particle size of cactus peels (Belayneh and Batu 2015).

Another strategy was developed by Hadjittotfi et al (2014) using fiber of cactus materials to produce biochar useful to remove Cu(II) from water. Cladodes were sundried, disintegrated, washed, dehydrated (70 °C), carbonization (200 °C for 30 min and 600 °C for 1 h), activated with nitric acid 12 M (24 h at room temperature and 3 h at 80 °C), washed with water, neutralized, dried (100 °C), grounded and sieved (200–500 μm). The biochar adsorption capacity reached 222 mg g⁻¹ (3.5 mol kg⁻¹) at pH 6.5, 25 °C, dosage of 6.7 g l⁻¹ and 24 h reaction time (Hadjittotfi et al 2014). Cr(II) removal was also investigated using phosphorylated (with 1.5 M H3PO4) and MnO2-coated cactus fiber samples and compared to untreated cactus fiber (Prodromou and Pashalidis 2013). Interestingly, the highest adsorption capacity (1.56 mol kg⁻¹) was obtained by MnO2-coated cactus fiber under optimal conditions (pH 6.5, 23 °C, 24 h reaction time and dosage 6.7 g L⁻¹) (Prodromou and
Pashalidis 2013). Likewise, the Cr(VI) removal ability by ectodermis (from Opuntia cactus) materials modified with formaldehyde or HCl was demonstrated in the work of Lopez-Gonzalez et al. (2012). The modified materials increase the Cr adsorption at pH 2 with value comparable to materials from other origins Lopez-Gonzalez et al. (2012). In the same context, the use NaOH and HCl enhance Zn and Mn sorption capacity of cladodes fiber. Zn removal passed from 36% (untreated cactus fiber) to 84.6% (after HCl treatment) and 95.9% (after NaOH treatment). However, for Mn, these values were 33.2%, 71% and 88.6%, respectively (Abhra et al. 2019). Removal enhancement may be contributed to the presence of the carboxylic group and the effect of the treatment which may enhance the surface available for metal sorption.

In the work of Vecino et al. (2016), biocomposites were formulated using gelling extract (obtained from O. ficus indica cactus mucilage), sodium alginate and calcium chloride. These materials allowed of 63% removal of As from contaminated water with an adsorption capacity of 101.6 mg g$^{-1}$ obtained at optimal formulation (Vecino et al. 2016).

The effect of the operating conditions including the contact time, adsorbent dose and temperature on the adsorption of Pb and Cd ions by cactus powder was performed by Derbe et al. (2015). Generally, Pb and Cd removal rates increase by rising the contact time and adsorbent dose. For example, the highest rates were obtained after incubation time of 120 min (58% for Pb and 43% for Cd) at a dose of 1 g l$^{-1}$. This fact is related to the end point at which adsorption phase reached the equilibrium. However, the temperature affects negatively the removal capability of cactus powder and significantly decreases both Pd and Cd removals, which could be explained by the physiosorption process. Moreover, it was reported that NaCl interact with the functional group of cactus powder limiting the adsorption of heavy metals and consequently metal removal capability decreases by increasing the NaCl dose (Derbe et al. 2015).

For many reasons (low cost, abundance, sustainability, reliability, renewable, environmental safety, etc), cactus materials ensure the environmental rules for the treatment of contaminated water with heavy metals. This ability involves chemisorption exchange between metallic ions and functional group including mainly carboxyl, carbonyl and hydroxyl groups present in cactus materials as demonstrated by spectroscopic studies. In some cases, cactus materials can be easily used as biosorbent without chemical addition. At the same time, various preparations using high temperature and chemicals were evaluated. The majority of experiments were conducted to remove heavy metal from aqueous solution. As far as we know, few data describing the employment of cactus based-biorsorbents for heavy metal elimination from real wastewaters was reported. For example, Fe and Cr were significantly reduced at acceptable levels while treating tannery wastewater using sun-dried cactus cladodes (Swathi et al. 2014).

Generally, the results presented in this review confirm that biosorbents obtained from cactus materials exhibit reasonable heavy metal adsorption capacity while compared to many other cheap materials (table 3). However, variations among results can be explained by the used biosorbent preparation processes and by the operating conditions (biosorbent dose, heavy metal initial concentration, pH, temperature, contact time, etc), which varied between experiments. Hence, is very important to point out the importance of the operating conditions, which should be optimized for each material used as biosorbent. Generally, pH is an important parameter that control the biosorption process (Barka et al. 2011). According to the literature, there is no range or fixed value of pH at which the maximum adsorption capacity is attained, and this is related to the nature of adsorbent materials and the adsorbate. The difference in biosorption trend for the same pH range may be attributed to the differences in behaviour among metals and their ions in solution. Also, the pH affects the speciation of the metal (metal distribution, precipitation and complexation), its stability and the chemical state of its reactive groups (protonation/deprotonation) (Fernandez-Lopez et al. 2014). Interestingly, the removal efficiency of metals is highly dependent on the quantity of the biosorbent. The initial dose is a key parameter to overcome mass transfer resistance between the aqueous and solid phases. Moreover, the removal rate increases with the increasing of adsorbent mass until an appropriate dose, and further increasing did not show any significant change on heavy metal removal. This due to the fact that active site of the biosorbent materials already occupied by adsorbent and the solution reaches equilibrium between the heavy metals and the used biosorbent materials (ALOthman et al. 2013)). Also, the particle size of the materials influences slightly the biosorption process. The decrease in particle size increases the biosorption yield at equilibrium. Small particle size allowed higher biosorption capacity. This could be explained by the fact that smaller particles offer larger surface area of the biosorbent (Barka et al. 2013b). The effect of the contact time was also investigated by allowing the solution to agitate for different periods. Sufficient contact time and stirring rate allow good mass transfer by minimizing the boundary layer width involving the adsorbate and the adsorbent (Barka et al. 2011). Concerning the temperature effects, the decrease of the adsorption with temperature is due to the weak binding interaction between the active site of the used material and the metal ions which support physiosorption process (Derbe et al. 2015). Furthermore, increasing the temperature could cause more pores expansion that can lead to leaching the heavy metal adsorbed (Uwah et al. 2013).
4. Dye removal

Different industrial activities discharge large quantity of coloured effluents in the environment, which may cause health and ecological problems as reported above. Human health problems varied depending on dye nature, time contact and concentration. In the aquatic environment, dyes avoid light penetration decreasing the photosynthetic activities (Hassaan and El Nemr 2017). Generally, dyes such as azo dyes are found to be toxic for flora and fauna. They cause the decline of microorganisms in soil affecting the agricultural activities. Dyes were also recognized by their poisonous and mutagens effects on organisms. To reduce the harmful impact of water polluted with chemical colorants, various treatment processes were commonly applied by the industries. These treatments included the coagulation-floculation, bioprocess, membrane filtration, advanced oxidation and adsorption (Venkatesh et al 2017, Robinson et al 2000). Recently, the adsorption technique is frequently used and many researches were done in order to select a new suitable material useful as absorbent. In this context, various preparations of cactus materials (fruit peel, mucilage and cladodes) were evaluated as biosorbents for decolorization. Interestingly, cactus based biosorbents exhibit very high maximum adsorption capacities when applied for the dyes removal from aqueous solution or from real wastewaters. Before use, cactus materials were subject to treatments including simple sun- dehydration, heat treatment and/or chemical treatments. As reported in table 4, sun-dried cactus cladodes were subject to dehydration at 60 °C (for 24 h) before being used for decolorization of solutions containing Methylene Blue, Eriochrome Black T and Alizarin S. Depending on

| Adsorbents | Adsorption capacity (mg/g) | References |
|------------|----------------------------|------------|
| Arsenic    |                            |            |
| Cactus mucilage | 0.14–2.8 | Fox et al 2012 |
| Cactus mucilage | 101.6 | Vecino et al 2016 |
| Cactus mucilage | 97.1 | Vecino et al 2016 |
| Sorghum    | 2.7 | Baig et al 2010 |
| Human Hairs | 0.01 | Mamishebei et al 2009 |
| Hexavalent Chromium |          |            |
| Cactus cladodes | 18.51 | Fernandez-Lopez et al 2014 |
| Cactus fruit ectodermis | 16.43 | Fernandez-Lopez et al 2014 |
| Cactus fruit ectodermis | 15.2–30.1 | Lopez-Gonzalez et al 2012 |
| Ficus carica fiber | 19.68 | Gupta et al 2013 |
| Walnut hull | 98.13 | Nurchi and Villaescusa 2008 |
| Saw-dust | 41.5 | Gupta and Babu 2009 |
| Pinus silvestris | 238.10 | Ucun et al 2008 |
| Almond green hull | 2.04 | Sahranavard et al 2011 |
| Cadmium(II) |              |            |
| Cactus cladodes | 30.42 | Barka et al 2013b |
| Cactus fruit peel | 14.03 | Keshri et al 2017 |
| Wheat bran | 62 | Yao, et al 2012 |
| Spent grain | 17.30 | Li et al 2010 |
| Scolymus hispanicus L. | 54.05 | Barka et al 2010 |
| Flammulina velutipes |         | Zhang et al 2010 |
| Lead(II) |              |            |
| Cactus cladodes | 98.62 | Barka et al 2013b |
| Spent grain | 35.5 | Li et al 2010 |
| Wheat bran | 21 | Yao et al 2012 |
| Citrus peels | 480.7 | Nijkam and Schiewer 2012 |
| Flammulina velutipes | 14.34 | Zhang et al 2010 |
Table 4. Examples of cactus material-based biosorbents for heavy dye removal.

| Cactus material-based biosorbent preparation | Removal efficiency (Y in %)/biosorption capacity (Q in mg/g) | References |
|---------------------------------------------|----------------------------------------------------------|------------|
| Cactus cladodes sun dried (3 weeks), cutted, dried at 60 °C (24 h) and powdered | Q: 189.83 mg/g for Methylene Blue Q: 200.22 mg/g for Eriochrome Black T Q: 118.35 mg/g for Alizarin S | Barka et al 2013b |
| Fruit peels: dried and treated with H₂SO₄ (1 M) and NaClO₃ (1 M) | Q: 167 mg/g for Brilliant Green (at pH 3 and 20 °C) | Kumar and Barakat 2013 |
| Natural cladodes of O. ficus indica, crushed, sieved (< 40 μ) Dried cladodes of O. ficus indica, crushed, sieved (< 40 μ) | Q: 3.44 mg/g for Methylene Blue, Langmuir Q: 10.04 mg/g for Methylene Blue, Langmuir | Sakr et al 2019 |
| Cactus fruit: dried (40 °C, sunlight, 15 days) washed several times (H₂O), dried at 40 °C, ground and sieved (< 315 nm) | Q: 222.22 mg g⁻¹ for Methylene Blue, Langmuir | Seghier et al 2017b |
| Activated carbon from cellulose waste, old cactus cladodes of O. ficus indica Activated carbon of prickly pear seeds of O. ficus indica after oil extraction. | Q: 750 mg/g for Methylene Blue (contact time 30 min) Q: 1200 mg/g for Methylene Blue (contact time 30 min) | Ouhammou et al 2019 |
| O. ficus indica cladodes: washed, air-dried, re-dried (105 °C, 48 h), ground and sieved | Y: 61% for Methylene Blue at room temperature, Freundlich | Sakr et al 2015 |
| O. ficus indica cladodes: dried at low temperature and powdered | Q: 198.9 mg/g for Acid Orange 51 Q: 45 mg/g for Reactive Red, Langmuir | Louati et al 2018 |
| O. ficus indica fruit: washed, cutted, sun dried and stove dried (313 K, 24 h) and sieved (0.84–2 mm) | Q: 188.7 mg/g for Basic Blue 9, Langmuir | Pelaez-Cid et al 2013 |
| O. ficus indica fruit: dried, activated (NaClO₃ 12%, 323 K), cooled, washed (H₂O), dried at (313 K, 24 h) and sieved (0.84–2 mm) | Q: 277.8 mg/g for Basic Blue 9, Langmuir | Pelaez-Cid et al 2013 |
| O. ficus indica fruit: dried, activated (NaOH 25%, 323 K), cooled, washed (H₂O), dried at (313 K, 24 h) and sieved (0.84–2 mm) | Q: 34.6 mg/g for Basic Blue 9, Langmuir | Pelaez-Cid et al 2013 |
| Cactus pear seed cake: dried (110 °C, 24 h), crushed, sieved (< 200 μ), activated (H₃PO₄, 85%), 60 °C, 1 h, dried (110 °C, 12 h), carbonization (400–600 °C, 1–2 h), washed (H₂O, pH 6–7), dried (110 °C, overnight) and ground (< 100 μm). | Y: 56.48% and Q: 260 mg/g for Methylene Blue (dosage 0.2 g l⁻¹, 20 °C, pH 7, contact time 180 min), Freundlich Y: 100% and Q: 336.12 mg/g for Methyl Orange (dosage 2 g l⁻¹, 20 °C, pH 7, contact time 180 min), Freundlich | El Magana et al 2019 |
| Palm cactus: ground, sieved (<0.2 mm), washed with ethanol (60% v/v, 343 K, 2 h), washed (H₂O) and dried (333K, 8 h) | Q: 173–220 mg/g for Crystal Violet | Pang et al 2019 |
| Fruit peels (O. ficus indica): sundried, cutted, activated with H₃PO₄ (85.5 v/v, 24 h), carbonization (673 K, 3 h), washed (H₂O), dried (393 K, 38 h), ground and sieved (0.25–0.841 mm) | Y: 76%–99% for textile effluent Q: 294 mg/g for Indigo Carmine, Langmuir Q: 909 mg/g for Solophenyl Blue, Langmuir Q: 416 mg/g for Methylene Blue, Langmuir Q: 312 mg/g for Crystal Violet, Langmuir | Pelaez-Cid et al 2016 |
| Cactus fruit peel: boiled in distilled water, sun-dried (20 days), washed (H₂O), dried (40–50 oC) and crushed (< 0.315 mm) | Y: 94% and Q: 151.51 mg/g for Acid Red dye from textile industry, Langmuir | Seghier et al 2017a |
| Cladodes of Tacinga palmadora: cutted (10 cm size), dried (50 C, 96 h), milled, sieved (<0.20 mm), washed with ethanol (60% v/v, 70 °C, 2 h), washed (H₂O) and dried (60 °C, 36 h) | Q: 228.74 mg/g for Crystal Violet (dosage 0.5/l, 55 °C, pH 10), Langmuir Y: 93% for simulate effluent (dose: 4.5 g l⁻¹) | Georgin et al 2019 |

pH, the biosorption capacity reached 190 mg g⁻¹, 118 mg g⁻¹ and 200 mg g⁻¹ respectively for Methylene Blue (at pH basic), Eriochrome Black T (at pH acid) and Alizarin S (at pH acid) (Barka et al 2013b). Advantageous results were also obtained with activated carbon obtained using cladodes (activation with phosphoric acid at 450 °C) while applied for the removal of Methylene blue and Iodine (Ouhammou et al 2019). In addition to cladodes, cactus fruit peel was subject to various treatments. For example, fruit peels sample was boiled in distilled water, sun-dried (20 days), washed with bidistilled water, redried (40–50 °C) and crushed (< 0.315 mm). The obtained powder showed high potential as biosorbent for Methylene blue, with sorption capacity of 222 mg/l (Seghier et al 2017b). Likewise, an efficient biosorbent was obtained by treating dried fruit peels with sulfuric acid (1 M) and sodium perchlorate (1 M). The allowed Brilliant Green adsorption capacity achieved 167 mg g⁻¹ at 20 °C and pH 3 (Kumar and Barakat 2013). Similarly, sodium hydroxide and sodium perchlorate was also used to treat separately other fruit peel samples. Interestingly, sodium perchlorate and sodium hydroxide enhanced significantly the removal rate (up to 96%) of basic dye and anionic dye, respectively.
Table 5. Comparative table of the maximum adsorption capacity of cactus material with other materials and for crystal violet and methylene blue.

| Adsorbent based materials             | Adsorption capacity (mg/g) | References                        |
|---------------------------------------|----------------------------|----------------------------------|
| Crystal violet                        |                            |                                   |
| Cactus fruit peels (treated with H₃PO₄) | 312                        | Pelaez-Cid et al 2016             |
| Palm cactus (treated with ethanol)     | 173–220                    | Pang et al 2019                   |
| Leaves of cactus (Tacinga palmadora)   | 228.74                     | Georgin et al 2019               |
| Elephant grass                        | 4.8                        | Aniagor and Menkiti 2018         |
| Ginger waste                          | 277.7                      | Kumar, Ahmad (2011)              |
| T. arjuna sawdust waste               | 46                         | Shakoor and Nasar 2018           |
| Rice husk (treated with NaOH)         | 293.30                     | Chakraborty et al 2011           |
| Sapindus mukorossi biomass            | 28                         | Samal et al 2019                 |
| Methylene blue                        |                            |                                   |
| Cactus fruit peels (treated with H₃PO₄) | 416                        | Pelaez-Cid et al 2016             |
| Cactus pear seed cake (treated with H₃PO₄) | 260                      | El Maguana et al 2019            |
| Cactus cladodes (activated carbon)     | 750                        | Ouhammou et al 2019              |
| Cactus prickly pear seeds (free of oil)| 1200                      | Ouhammou et al 2019              |
| Cactus cladodes (without treatment)    | 3.44                       | Saker et al 2019                 |
| Cactus cladodes (dried)               | 198.83                     | Barka et al 2013b                |
| Cactus fruit peel                     | 222                        | Seghier et al 2017b              |
| Black stone cherries                  | 321.75                     | Arana and Mazzocco 2010          |
| Walnut shell                          | 315                        | Yang and Qiu 2010                |
| Hazelnut husks                        | 204                        | Ozor et al 2012                  |
| Plant leaf powder                     | 61.22                      | Gunasekar and Ponnusami 2012     |
| Wood apple rind                       | 40                         | Malavizhi and Ho 2014            |

(Pelaez-Cid et al 2013). Using other preparation methods, granular activated carbon was prepared using cactus pear peels. In this process, cactus residue was sun-dried, cut down to strips and activated with phosphoric acid for 24. After carbonization (673 K, 3 h), the material was washed with water, dried (393 K, 38 h) and grounded. The obtained materials were applied to remove various dyes (Methylene Blue, Solophenyl Blue, Indigo Carmine and Crystal Violet) from water. Based on Langmuir isotherms, the obtained granular activated carbon with size (0.25–0.841 mm) reached adsorption capacity ranged of 284 mg g⁻¹ (for Indigo Carmine), 909 mg g⁻¹ (for Solophenyl blue) and 416 mg g⁻¹ (for Methylene blue.) These results were comparable to that obtained for white sapote seeds and broccoli stems (Pelaez-Cid et al 2016). Interestingly, these materials were also useful for textile wastewaters with removal rates (76%–90%) comparable to that obtained with commercial powdered carbon (Pelaez-Cid et al 2016). In the same context, a real tannery wastewater was used to perform the feasibility of dried cladodes adsorbent as treatment option. The cactus material was able to remove up to 70% of both COD and BOD, 90% of sulphate and 98% of iron. In addition to that, it was demonstrated that the biosorbent capacity tolerates pH ranged from 6 to 10 and increases with working temperature (Swathi et al 2014). More recently, dried and powdered biomass of Tacinga palmadora cactus showed decolorization rate of 93% (adsorption capacity of 228.74 mg g⁻¹) from simulated textile wastewater loaded with crystal violet. This result was obtained with adsorbent dose of 0.5 g L⁻¹ and at pH 10 (Georgin et al 2019). Nevertheless, it is very important to point out the increase of dye sorption by the dosage allowing high number of reactive vacant sites, high transfer and high gradient concentration (Ghaedi et al 2015).

Generally, cactus based-material offered an adsorption ability comparable to other biosorbents as summarized in table 5. This indicates that adsorbents prepared from cactus are useful for the removal of various dyes, with fast kinetics (Georgin et al 2019). However, decolourization rates are managed by various parameters such preparation methods and the operating conditions (pH, temperatures, contact time, dosage, etc) as reported for heavy metals. However, the pH remains the most important factors affecting dye adsorption. Depending on dye nature, high pH is favorable for cationic dye adsorption and low pH is favorable for anionic dye adsorption. Moreover, the pH affects the surface behavior of the adsorbent (Salleh et al 2011). Consequently, it is important to optimize the pH value for each adsorption experiments.

As reported for heavy metals, functional groups of cactus are involved in the sorption process. Furthermore, chemical treatments permit the conversion of cactus functional group, which may enlarge the biosorbent specific surface area (Kumar and Barakat 2013, Pelaez-Cid et al 2013). Each activated cactus material is marked by its particular pore surface and its index of adsorption. The two properties varied depending on the activation methods and on the used biomass. Although the similarity in structure, rigidity and porosity, differences were observed while compared cactus to other materials (such as date, pumpkin seed shell, etc) (Li et al 2015).
5. Conclusion

This study summarized recent reports in which cactus materials (cladodes, fruit seeds, peel, etc) have been employed to produce efficient adsorbents. Cactus-based biosorbents were prepared using various methods including heat and chemical treatments. The obtained materials (untreated, sun-dried, thermally and chemically treated materials) were tested for decolorization and metal removal. The removal efficiency and biosorption capacity were controlled by various factors including the preparation methods, the pollutant subject to removal and the operating conditions (dosage, pH, temperature, contact time, etc). Based on the experimental data, promising removal efficiencies were observed for both heavy metals and dyes. Generally, kinetic results fit well with Langmuir isotherm. However, the majority of experiment was conducted for pollutants in aqueous solutions and only few data dealing with real wastewater were reported. Therefore, more researches are needed to evaluate the process efficiency using real wastewater at large scale. Moreover, in order to evaluate the competitive applicability of cactus materials, economical and environmental study should be addressed taking in consideration the adsorbents properties (alteration, bacterial degradation, regeneration, life cycle, etc) and the disposal of the generated wastes including the loaded pollutants and chemical related to the adsorption/desorption process.

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