Chapter 9
Application of Date-Palm Fibres for the Wastewater Treatment

Marija Nujic, Natalija Velic, and Mirna Habuda-Stanić

Abstract Many industries produce large quantities of wastewater. Effluents discharged from industries are often highly polluted and could be toxic to aquatic life. Recently, alternative methods for wastewater treatment have been extensively researched. Removal of different pollutants by adsorption on lignocellulosic materials proved to be a promising, cost-effective method. Large amounts of lignocellulosic materials are produced daily as waste materials of agri-food and wood industries, and large portion ends up on landfills. Such wastes are cheap and often available throughout the year, so their applications as adsorbents have multiple advantages: (i) waste decline and (ii) pollutant removal from wastewater.

This chapter explores the use of date-palm fibres as low-cost adsorbent in wastewater treatment processes. Studies have shown that date-palm based adsorbents have the capability to remove various pollutants such as dyes, heavy metal ions and phosphates. Furthermore, the review provides important information about the adsorption capacities and the utility of date-palm fibers used as adsorbent for pollutant removal from wastewater.

Keywords Adsorption · Date-palm fibres · Pollutants removal · Dyes · Heavy metals

9.1 Introduction

The protection of different ecosystems presents a huge challenge for scientists and engineers in times of intense technology development and population growth, especially in developing countries (Ahmad et al. 2012). As a result of their characteristics and the amounts released to the water bodies, pollutants can detrimentally affect human health, flora and fauna, biodiversity, as well as landscape diversity

M. Nujic (✉) · N. Velic · M. Habuda-Stanić
Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, Osijek, Croatia
e-mail: marija.nujic@ptfos.hr

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(Naushad and Alothman 2015; Alqadami et al. 2016). Therefore, it is necessary to remove them from water bodies, or preferably remove them from wastewaters before the discharge to natural recipients. The increase in volume of industrial wastewater is evident in developing countries and can be related to the population growth (Gobi and Vadivelu 2013). Reports and statistics showed that 70% of freshwater consumption is related to food processing and irrigation. In addition, many pollutants can occur in groundwater and deteriorate its physical-chemical quality. In contrast, in developing countries over 70% of industrial waste is disposed without treatment, and about 90% of wastewaters enters rivers and lakes untreated (Wong et al. 2018).

The wastewater treatment is an integral part of water protection and, therefore, a subject of numerous researches with the collective aim to find new, effective and cost efficient treatment technologies (Awual et al. 2016; Naushad et al. 2016). Heavy metal ions and organic compounds in water for human consumption can cause different problems. For example, phenols can accelerate tumour formation, sulphates cause dehydration, and chromium can cause the formation of different carcinomas (Alshehri et al. 2014; Kumar et al. 2016). Dye loaded wastewaters can have a negative impact on the biota (Alghamdi 2016). There are a number of technologies available for water pollution control, such as filtration, oxidation, chemical precipitation, reduction, ion exchange, adsorption, membrane separation and many more (Ahmad et al. 2011). However, these methods have limitations such as oxidation by-products formation, sludge generation, regeneration of ion exchangers, membrane fouling, high energy cost etc. (Amin et al. 2017). Because of its simple operation, versatility and high efficiency, adsorption is often the method of choice for different pollutants removal from aqueous media.

Recently, researchers have shown an increased interest in alternative methods for pollutants removal from wastewater, including adsorption onto low-cost adsorbents, which are widely distributed, locally available and cheap (Belala et al. 2011). The applicability of waste lignocellulosic materials as adsorbents is achieved by the interaction of adsorbents with functional groups present in these materials (*e.g.* –OH and –COOH). These functional groups are mostly common to all lignocellulosic materials, but their number depends on the type of material. In order to modify the surface of the adsorbent, or to increase the number of functional groups available for adsorption processes, various modification methods of lignocellulosic waste material were investigated, such as modification with inorganic and organic acids (HCl, HNO_3, H_2SO_4, CH_3COOH, $CH_3CH(OH)COOH$, HCOOH), alkali and solutions (NaOH, $Ca(OH)_2$, $CaCl_2$, Na_2CO_3), and many other inorganic and organic compounds (formaldehyde, glutaraldehyde, methanol, epichlorohydrin) (Abdolali et al. 2014) (Fig. 9.1).

These adsorbents have been used for different water pollutants removal: metal ions, dyes, phenols, pesticides, polychlorinated biphenyls etc. (Ofomaja 2007). Various low-cost adsorbents (biosorbents) were investigated for dye removal, such as spent grain (Kezerle et al. 2018), cashew nut shell (Spagnoli et al. 2017), sunflower stalks (Sun and Xu 1997), wood sawdust (Suteu and Zaharia 2011), orange peel (Annadurai et al. 2002), palm-fruit bunch (Nassar et al. 1995), banana pith (Namasivayam et al. 1993), maize cobs (El-Geundi 1991), and others. Metal

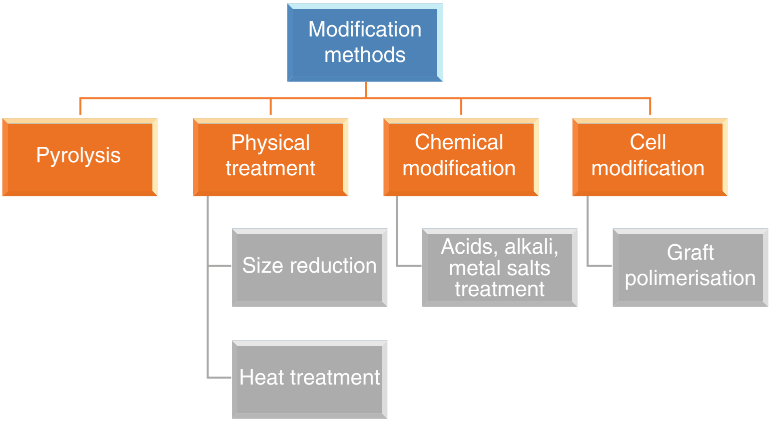

Fig. 9.1 Modification methods of waste lignocellulosic materials. (According to Nguyen et al. 2013)

ions adsorption onto biosorbents was also studied: spent grain (Li et al. 2012), brown seaweed (Uzunoğlu et al. 2014), okra, pumpkin, grape and squash seeds (Al Bsoul et al. 2014), lentil, wheat and rice shells (Aydin et al. 2008), etc. Date palm fibres (DPFs) have been investigated for the adsorptive removal of both, dyes and metal ions (Al-Haidary et al. 2011; Alshabanat et al. 2013), which is presented in this work.

9.2 Date Palm Fibres as Low-Cost Adsorbents

Low-cost lignocellulosic waste materials, offer some advantages for the removal of pollutants from water: porosity, high surface area and resistance to biological degradation. In addition, using waste materials as adsorbents and the development of technologies that incorporate raw materials is an important alternative for pollution control (Bryan and Daniella 2012; Kharat 2015; Alghamdi 2016).

Lignocellulosic materials consist of three polymers: cellulose, hemicellulose and lignin (Al-Kaabi et al. 2005). Besides these polymers, lignocellulosic wastes contain smaller amount of water, ash, cyclic carbohydrate and organic or inorganic extractives (Cagnon et al. 2009). Date-palm fibres (DPFs) have four types of fibres, namely, leaf fibres in the peduncle, baste fibres in the stem, wood fibres in the trunk and surface fibres around the trunk (Khidir et al. 2014; Alghamdi 2016) which make them potentially efficient adsorbents. So far, the research has been conducted using date-palm fibres for dye removal (crystal violet malachite green, Congo red, Rhodamine B6), metal ions removal (Cd, Pb, Cu, As) and phosphate removal.

Date-palm wastes as biosorbents are considered to be efficient for the removal of various pollutants from wastewater, but are particularly effective for the removal of heavy metal ions (Shafiq et al. 2018). Since large amounts of DPFs wastes are disposed unutilised, they have an economic and environmental potential to be valorised in wastewater treatment (Riahi et al. 2009a).

9.2.1 Removal of Synthetic Dyes from Wastewater Using Date Palm Fibres

Wastewaters containing high concentrations of dyes, are usually rich in organic content as well. Such wastewaters, after being discharged into the environment, can be harmful to aquatic life (Lee et al. 1999; Kadirvelu et al. 2001). Synthetic dyes are used in many industries. However, they are the most extensively used in textile, paper, leather and plastic industries, which are thus recognised as the main sources of dye-loaded effluents (Gouamid et al. 2013).

The adsorption of crystal violet (CV) on DPFs was studied by Alshabanat et al. (2013). DPFs were milled and sieved to obtain fine particles. About 0.25 g of adsorbent and 25 mL of CV model solution in concentration range of $0.9{\cdot}10^{-5}$–$7{\cdot}10^{-5}$ mol L^{-1} was used in the experiments. The impact of temperature and pH on adsorptive CV removal was also tested. All experiments were conducted at 25 °C and 100 rpm. The experimentally obtained data were fitted to Langmuir, Freundlich, Elovich and Temkin isotherm models. The results revealed that DPFs are a promising adsorbent for CV removal in a wide concentration range. Additionally, the adsorption of CV on DPFs was best described by Elovich model and the maximum adsorption capacity was equal to the experimental value. Higher removal percentage was achieved at lower temperatures and pH. Thermodynamic analysis showed that the interaction between CV and DPFs was exothermic and spontaneous, and the pseudo-second-order kinetic model gave a better fit with the experimentally obtained data. In another study, Alshabanat, Al-Mufarij, & Al-Senani (2016) examined the adsorption of malachite green (MG), an extensively used dye in textile industry, onto DPFs. The adsorption isotherms showed that the adsorption was more efficient with the increment of MG concentration in solution. The percent removal of dye increased (about 92–95.5%) with the increase of the dye solution pH (from 4 to 10). With the increase of temperature from 25 to 45 °C, the percent removal of dye decreased. Kinetic study revealed that the pseudo-second-order model showed a better fit than the pseudo-first-order model.

Belala et al. (2011) investigated the effect of contact time, temperature, and dye concentration on the adsorption process of methylene blue (MB) onto palm-trees waste. The recorded FTIR spectrum of the biosorbent indicated different functional groups (hydroxyl, carboxyl and carbonyl) that probably serve as the potential adsorption sites for MB. The effect of contact time was tested for the initial MB concentration of 100 mg L^{-1} and biosorbent concentration of 10 g L^{-1}. Results showed that the adsorption capacity increased with the increase of adsorption time and reached the equilibrium at 150 min. The adsorption was very rapid within the first 40 min and then slowed down until equilibrium was reached. In addition, the results showed that the adsorption improved with the increase of adsorption

Fig. 9.2 Chemical structure of methylene blue

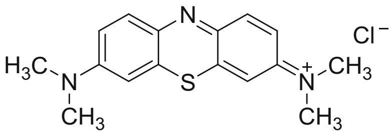

Table 9.1 Date palm biomass for dye removal from aqueous solutions

Adsorbent	Dye	q_{max}	References
Palm-trees waste	Methylene blue	39.5 mg g^{-1} (Langmuir)	Belala et al. (2011)
Date palm leaves	Methylene blue	58.14 mg g^{-1} (Langmuir)	Gouamid et al. (2013)
Date-palm fibre	Methylene blue	5.02 mg g^{-1} (Langmuir)	Mahmoud (2013)
Date-palm fibre	Crystal violet	12.02 mol g^{-1} (Temkin)	Alshabanat et al. (2013)
Date-palm fibre	Malachite green	0.21 mol g^{-1} (experimental)	Alshabanat et al. (2016)

temperature. The linearized Langmuir model was in a better agreement with experimentally obtained data, compared to linearized Freundlich and Temkin isotherm models, which suggests a monolayer coverage of the surface of adsorbent by MB (Belala et al. 2011). The structure of MB dye is given in Fig. 9.2.

There has been an attempt to remove MB from aqueous solution using date palm leaves. Gouamid et al. (2013) conducted the adsorption experiments in a batch process with adsorbent concentration of 1 g L^{-1} and MB solution of 200 mg L^{-1} at pH ranging from 2 to 8. Results revealed that the highest adsorption efficiency was achieved at pH 6.5. Four isotherms models have been used to analyse the experimentally obtained adsorption data: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. The Temkin isotherm proved to be the best. Kinetic studies revealed that MB is slowly transported via intraparticle diffusion into the particles and is finally retained in micropores.

The study on MB adsorption on DPF was conducted by Mahmoud (2013) with the initial MB concentration from 50 to 150 mg L^{-1}. The results revealed that the amount of MB adsorbed increased from 4.82 to 12.25 mg g^{-1} at solution pH 7.5 and 30 °C. The percent removal of MB was in the range from 94% to 98% at temperatures from 30 to 60 °C and at pH from 6 to 8. The effect of particle size was also assessed: the adsorption of MB increased with the decrease in particle size. In addition, the Langmuir isotherm model fitted best (q_{max} = 5.02 mg g^{-1} at 60 °C) with initial MB concentration of 50 mg L^{-1} A comparison of the adsorption capacities using date palm biomass for dye removal are presented in (Table 9.1).

9.2.2 *Removal of Metal Ions from Wastewater Using Date Palm Fibres*

Different process parameters affect the adsorption of heavy metal ions: contact time, pH, dose and size of adsorbent, initial metal ion concentration, modification of adsorbent, *etc*.

The adsorption of copper, lead and arsenic on DPFs was examined by Amin et al. 2017). The DPFs were immersed in water and then separated into individual fibres (0.2–0.8 mm diameter). After that, the DPFs were washed with distilled water for 30 min and filtered, dried at 105 °C for 24 h and then crushed in a crushing machine. Kinetic experiments were conducted at following conditions: initial metal concentration of 20 mg L^{-1}, pH 5, adsorbent concentration of 0.5 g L^{-1} and particle size of 152 μm. The results showed that high adsorption capacities were achieved within first 90 min, while the slower metal uptake occurred for the next 30 min of 120 min contact time for all three metal ions (Cu, Pb and As). The adsorption data showed a linear increase in metal removal capacities with increasing DPFs concentration from 0.1 to 2 g L^{-1}. With increase of initial metal ion concentration from 20 to 80 mg L^{-1}, the removal percentage decreased 30–40% due to saturation of sorption sites on the surface of DPFs.

Amin et al. (2016) investigated the use of date-palm trunk fibres as biosorbent for copper ions removal from aqueous solution. The copper adsorption was dependant on the adsorbent particle size, where the highest adsorption capacity of 34 mg g^{-1} was achieved when 75 μm adsorbent particle was used. Furthermore, with the increase of Cu^{2+} concentration from 20 to 100 mg L^{-1}, the adsorption capacity also increased from 6 to 23 mg g^{-1}. The behaviour and nature of copper ions adsorption was analysed with Langmuir, Freundlich, Harkins-Jura and Dubinin-Radushkevich isotherm models. The experimental adsorption data were analysed using the appropriated isotherm models that fitted the data in the following order: Langmuir > Harkins-Jura > Freundlich > Dubinin-Radushkevich. The results indicate the monolayer copper adsorption. The experimental kinetic data were best described with the pseudo-second-order kinetic model, suggesting that surface modifications could improve the adsorption characteristics of date-palm trunk fibres as biosorbent (Amin et al. 2016).

Based on the results of their investigation, Yadav et al. (2015) concluded that date-palm trunk fibres could remove up to 99.95% of Cr (VI) from a 100 mg L^{-1} solution using only 1.2 g L^{-1} adsorbent. In a case of Pb(II) removal, the adsorption was quick and equilibrium established within 120 min (Yadav et al. 2013).

DPFs as adsorbents for lead removal from water were tested by Hikmat et al. (2014). This research also investigated the removal of lead ions using leaf base (petiol) waste. The results revealed that the adsorption equilibrium time was 30 and 40 min for Pb(II) by leaf and DPFs, respectively. In addition, an increase of lead uptake was observed in a pH range of 6.5–7 with adsorbent dose of 0.5 g. The thermodynamic parameters showed exothermic and spontaneous adsorption process. The removal percentage was 98.4% (q_{max} = 21.83 mg g^{-1}) and 96.5%

(q_{max} = 22.98 mg g^{-1}) by leaf and fibre, respectively. Thus, it was concluded that the tested waste materials can be successfully used for lead ions removal.

Al-Haidary et al. (2011) tested DPFs and petiole for Pb(II) removal from wastewater. The results of batch adsorption experiments showed that the adsorption capacity increased as the contact time increased. The adsorption capacity was higher at pH 4.5 than in alkali media, which can be attributed to the lower competition between protons and Pb(II) ions at higher pH. In addition, the adsorption of Pb (II) onto used biosorbents proved to be dependent on adsorbent concentration and particle size, as well as on ionic strength (NaCl solution). Three isotherm models (Langmuir, Freundlich and Dubinin-Radushkevich) were found to be applicable. The kinetics followed the pseudo-second-order model.

The removal of chromium using acid treated DPFs (0.1 M HCl, 8 h) was investigated by Hossini et al. (2016). A several parameters were investigated: the influence of pH, initial chromium concentration and biosorbent concentration. It has been shown that maximum chromium removal of 95% was achieved at pH 3.3, initial chromium concentration of 180 mg L^{-1} and biosorbent concentration of 0.8% (w/v) (particle size between 200 and 300 mesh size). The sorption kinetics showed good fit with pseudo-second-order model with tendency of fast adsorption. According to Langmuir isotherm model, the monolayer adsorption was suggested.

The adsorption of Cr(VI) onto DPFs (leaf) was investigated by (Haleem and Abdulgafoor 2010). The results revealed that the adsorption was pH dependent, with an optimum at pH 7. Also, at lower initial Cr(VI) concentrations, the removal percentage was higher. The adsorption data could be interpreted in terms of Langmuir isotherm model (adsorption capacity of 12.25 mg g^{-1}).

Rahmana et al. (2017) compared DPFs to commercially available adsorbents for chromium removal from aqueous solutions, and found DPFs to be better. The highest removal percentage was obtained at pH 2 (19.55 mg g^{-1}). The adsorption capacity increased with the increase of initial chromium concentration from 100 to 500 mg L^{-1} (from 9.84 to 57.26 mg g^{-1}), while the percent removal decreased from 98.44% to 57.26%. Furthermore, the increase of adsorbent concentration had also positively affected the chromium ions removal. The Langmuir isotherm model fitted the experimental adsorption data better than other models, thus confirming the monolayer adsorption. Table 9.2 shows the adsorption capacities of date palm biomass for metal ions removal.

The removal of Ni and Cd from wastewater with palm fibres powder has been studies by Boudaoud et al. (2017). The adsorption was pH dependent and the highest percent removal was achieved at initial metal ions concentration of 100 mg L^{-1}, 1 g of adsorbent, 20 °C and pH 5 (Ni) and 6.5 (Cd). The maximum adsorption capacities were 6.81 mg g^{-1} for cadmium at 60 min and 4.42 mg g^{-1} for nickel at 45 min. When these results are compared to adsorption capacities obtained using date palm seeds activated carbon for cadmium removal (0.0019 mg g^{-1}) (Nwakonobi et al. 2018), they proved to be much higher. The experimentally obtained data showed slightly better fit with Freundlich isotherm model. The $1/n$ values indicate that the adsorption process for both tested metal ions on the prepared adsorbent is a physical process. The pseudo-second-order model suggests that the adsorption is controlled

Table 9.2 Date palm biomass for metal ions removal from aqueous solutions

Adsorbent	Metal ion	q_{max}/mg g^{-1}	References
Date-palm fibre	As(V)	32.05 (Langmuir)	Amin et al. (2017)
Date-palm fibre	Pb(II)	18.416 (Langmuir)	Al-Haidary et al. (2011)
Date-palm fibre	Pb(II)	22.99 (Langmuir)	Hikmat et al. (2014)
Date-palm fibre	Cr(VI)	62.5 (Langmuir)	Rahmana et al. (2017)
Acid treateddate-palm fibre	Cr(VI)	34.12 (Langmuir)	Hossini et al. (2016)
Date-palm trunk fibre	Cu(II)	25.25 (Langmuir)	Amin et al. (2016)
Date-palm trunk fibre	Cr(VI)	129.87 (Langmuir)	Yadav et al. (2015)
Date-palm trunk fibre	Pb(II)	53.48 (Langmuir)	Yadav et al. (2013)
Date-palm fibre (leef)	Cr(VI)	12.25 (Langmuir)	Haleem and Abdulgafoor (2010)
Palm fibres powder	Ni(II)	4.42 (Langmuir)	Boudaoud et al. (2017)
Palm fibres powder	Cd(II)	6.81 (Langmuir)	Boudaoud et al. (2017)

by chemical process. The experimentally obtained adsorption capacities at equilibrium (6.486 mg g^{-1}) were in agreement with those calculated using the pseudo-second-order kinetic model (6.430 mg g^{-1}).

In the research performed by Ahmed (2010), wastes of date palm tree were used to remove heavy metal cations – Cu(II), Cd(II) and Zn(II) from wastewater by batch adsorption. The removal efficiencies were about 90% for Cu(II), 58% for Cd(II) and 38% for Zn(II) within 60 min of contact time and with adsorbent concentration of 30 g L^{-1}. The removal efficiency was lower in binary cation solutions.

9.2.3 Date-Palm Fibres as Filter Media

The application of DPFs as an efficient filter media for phosphorus, organic matter, turbidity and helminth eggs removal was investigated by Riahi et al. (2009a). Column experiments were performed under different experimental conditions such as flow rate, filter depth and diameter of the fibres. The results showed that the fibre diameter had a significant impact on the removal percentage. The filtration trough DPFs led to approximately 55% turbidity decrease, as well as 81% organic matter (as chemical oxygen demand – COD), 58% phosphorus and 98% of helminth eggs removal. The results showed that this technique has a potential to be used as economically feasible and environmentally friendly method for tertiary wastewater treatment.

DPFs as a laboratory filtration setup was employed for lead Pb(II) removal by Alghamdi (2016). It was observed that the breakthrough point was achieved after 3 min, which can be explained by the fact that the saturation rate of DPFs with lead ions was very quick. The recorded FTIR spectra showed that the adsorption of lead ions on DPFs was achieved by chemisorption in which mostly –OH groups were involved. The optimal flow rate was found to be 10 mL min^{-1} and initial Pb (II) concentration of 135 mg L^{-1}.

Ghazy et al. (2016) evaluated the performance of biofilters with various agricultural waste materials (rice straw, date-palm fibre, orange tree wood chips) for municipal wastewater treatment. Column experiments were performed under different operational conditions: hydraulic rates of 4.8, 6, 8 and 12 $m^3/m^2/d$ and medium size of fibres of 2, 4, 6 and 8 cm. The raw wastewater was pumped into the upper end of reactor and the effluent flowed out at the bottom of the reactor. The percent removal of the biological oxygen demand (BOD_5) was 81.5, 88.3 and 66.7% for rice straw, DPFs and orange tree wood chips, respectively. The results for chemical oxygen demand (COD) removal were 79.7% for rice straw, 88.3% for DPFsand 64.6% for orange tree wood chips. Total suspended solids (TSS), total nitrogen and total phosphorous were also determined. The investigation of the effect of the wood chip sizes of the used wastes as biofilters on the tested wastewater parameters showed that the smallest size was the most effective for all biofilter media, because it showed the best removal efficiency for wastewater contaminants (BOD, COD and TSS), while the largest size showed the lowest efficiencies for the tested parameters. The effect of column depth was also investigated. Four different depths were applied (20, 40, 60 and 80 cm), and it was shown that the highest removal percentage of BOD, COD and TSS was achieved at the depth of 80 cm, probably due to the increase in the total surface area and contact time between constituents and filter bed media. When comparing the hydraulic rates, the results showed that the lowest flow rate (4.8 $m^3/m^2/d$) showed the highest treatment efficiencies. In conclusion, the results showed that DPFs found to be the most efficient biofilter of all the tested materials, because it showed the best removal efficiencies for all tested parameters.

9.2.4 Removal of Other Pollutants from Wastewater Using Date Palm Fibres

Phosphates are often present in surface waters and wastewaters as organic phosphate, inorganic phosphate, oligophosphates and polyphosphates. They are extensively used in agriculture, as they are important nutrients for plants. However, excess concentrations in surface waters can have harmful effects to the environment, primarily eutrophication. Eutrophication of water bodies occurs if nutrients (nitrogen and phosphorus) are present in large amounts.

Riahi et al. (2009b) conducted a batch test to remove phosphates from aqueous solutions using DPFs. It was shown that the phosphate uptake increased with the increase of initial phosphate concentration and decreased with the increase of pH. The increase in adsorbent concentration also had a positive effect on phosphate removal. At pH 6.8, adsorbent concentration of 6 g L^{-1}, initial phosphate concentration of 50 mg L^{-1} and 18 °C, the adsorption capacity of phosphates was

4.35 mg g^{-1}, which makes this adsorbent potentially attractive for phosphate removal from water.

As it is already mentioned, phosphates in water are undesirable because they deteriorate the water quality. Granular date stones and palm surface fibres was used as biosorbents for phosphate removal from water by Ismail (2012). The percent removal of phosphates at initial phosphate concentration of 50 mg L^{-1} was 87% and 85% for granular date stones and palm surface fibres, respectively. The removal efficiency increased from 25% to 85% for palm surface fibres with the increase of biosorbent concentration from 1 to 10 g L^{-1}.

9.3 Conclusions

In this review, the use of date-palm fibre based biosorbents for the removal of different pollutants from aqueous solutions and/or wastewater have been reviewed. To date the literature on the use of this waste material as biosorbent is scarce. However, the existing data suggests that the date-palm fibres could be successfully employed as low-cost adsorbent for the removal of various pollutants from wastewater, such as synthetic dyes, heavy metals, organic matter and nutrients (phosphorus). Thus, date-palm fibers could present a good alternative to costly conventional adsorbents for water treatment, such as activated carbon. However, further research is needed to determine date-palm fibers feasibility as adsorbent on industrial scale. In addition, cost analysis needs to be performed, as well as the investigation of possible disposal methods of pollutant-loaded biosorbent left after adsorption removal process.

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