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BIOSORPTION OF LEAD FROM INDUSTRIAL WASTEWATER USING SOME PART OF DATE PALM TREES

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ABSTRACT

The lead removal capacity of the aqueous solution was examine with date palm trees (DPT). The effects of pH, contact time, temperature, and mixing speed on biosorption were investigate. The residual concentration of lead in aqueous solution was determine by the Atomic Absorption Spectrophotometer. The results of using the DPT Pinnae indicated that the optimal time was 50-90 min and high adsorption of Pb was at initial the 40 min, pH 6.5, 15 °C, and 100 rpm. Whereas DPT Blade showed, the optimal time was 60-90 min with high adsorption of Pb at first 20 min, pH 6.5, 15°C, and 100 rpm. While DPT Fiber, the equilibrium time was at 40-50 min with significantly high adsorption of Pb during the first 30 min, pH 5.5, 25 °C, and 50 rpm. The optimum parameters which studied in aqueous solution have been applied to remove heavy metals from industrial samples. The results showed high lead adsorption (0.2837mgg^{-1}, 37.68%), (0.3278mgg^{-1}, 41.11%) and (0.3934mgg^{-1}, 49.71%) for the DPT Pinnae, Blade, and Fiber, respectively. The functional groups of DPT were determined using the Fourier transform infrared (FT-IR) spectrophotometer analysis. The scanning electron microscope (SEM) confirmed the elimination of lead causing morphological changes.

KEYWORDS : Biosorption, Lead removal, DPT, FTIR, SEM

INTRODUCTION

Contamination of heavy metals is one of the toxicity, persistence, and bioaccumulation environmental issues (Mihajlovic *et al.,* 2015). Metal pollutants are most harmful due to their non-biodegradable nature and toxicity. In the field, these characteristics also make them very stable. The platinum, lead, cadmium, chromium, mercury, copper, arsenic, and antimony are of great importance through these metals (Hossain *et al.,* 2014). Toxic heavy metals are stable elements, even at very low concentrations; they can not be metabolized by the body and passed into the food chain. Lead in industrial wastewater is a major pollutant (Zhang *et al.,* 2005). Industrial wastewater with high concentrations of lead is introduce into mining water bodies, battery manufacturing, paint, pigments, coal combustion, etc. Therefore, the removal and recovery of heavy metals from wastewater streams are essential for the protection of the environment (Sheba and Nandini, 2016).Lead poisoning in humans causes severe damage to the liver, brain, kidneys, nervous system, and reproductive system. Long-term exposure can induce infertility, abortion, and neonatal death (Samra *et al.,* 2014).

Conventional approaches include chemical evaporation, membrane filtration, desalination, coagulation, and flocculation, ion replacement, electrodian and reverse osmosis (Amin *et al.,* 2016). Heavy metals were extracted from industrial wastewater. However, these approaches have many drawbacks, including high-energy costs, the development of by-products for oxidation. Moreover, in the case of heavy metal concentrations (100 mgl^{-1}) in an aqueous solution, these approaches are also unsuccessful (Rathinam *et al.,* 2011). Since then, a hunt has been undertaken for cheap and readily available adsorbents, leading to the study of agricultural and natural materials and industrial by-products, which can be used as adsorbents. Biosorption has strong advantages in relation to

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conventional processes because it is non-polluting and highly selective, reliable and easy to maintain and, therefore, cost-effective in treating large quantities of low-metal wastewater (Puranik and Paknikar, 1997). The technology has received considerable attention in industrial wastewater treatment, primarily because biological adsorbents, metal selectivity and metal recycling are available easily, and heavy metal is better absorbed and reused (Mandal, 2014). Some organic sorbents have a high sorption potential due to the existence of sufficient functional groups that are able to sequester metals with aqueous solutions (Edokpayi *et al.*, 2015). This technique is inexpensive, environmentally friendly and, of course, usable, these biological materials have shown a propensity to remove the metal traces, overcoming some of the major shortcomings in traditional processes (Gavrilescu, 2004).

Dating Palm Tree (DPT) biomass was of great importance among many agricultural waste products that have been investigated as adsorbents for the removal of pollutants since the components were studied extensively to remove various types of contaminants; agricultural wastes based on date palms have received a lot of attention as effective adsorbents due to its low cost and meaning.

DPT is known to be the best biosorbent to remove both wastewater and industrial wastewater effluents, but is especially efficient in heavy metal removal (Shafiq, 2018). The development of new eco-friendly wastewater treatment technologies has been encouraged. The purpose of this work was to stress the use of certain parts of the date.

MATERIALS AND METHODS

Sample collection

Samples of the date palm tree (Pinnae, Blade and Fiber) were collected from Basra-Iraq. They were put in clean plastic and transported to the laboratory.

Adsorbent

In order to prepare the adsorbent, they were washed with distilled water and placed on a clean table to dry at room temperature. Then they were crushed and grounded with a grinder. After grounded, they were sieved using 60 μ mesh sizes. The leaves were dried by dry heating at a temperature of 100 °C until they reached a constant weight (Mohammadi *et al.*, 2017).

Adsorbate

The stock solution was prepared by dissolving 1000 mg of lead in one liter of distilled water, and then a concentration of 25 mg L^{-1} was prepared by progressive dilution of stock lead solutions using distilled water. The pH of the solution was adjusted to 4.5-8.5 by the addition of 0.1M HCl or 0.1M NaOH solution.

Biosorption studies

Pb adsorption was studied in multiparameter batch experiments including time of contact, pH, temperature and speed of mixing (rpm). 50 mg of biosorbent was placed in Erlenmeyer flasks size 250 mL with 15 mL of lead ion solution of the desired concentration. The mixture was stirred at (15- 55)°C and 50- 200 rpm. The contact time varied from zero to 90 min. at a predetermined time. Then it filtered through Whitman filter paper No 40. The measurement of lead residues was carried out using an Atomic Absorption spectrophotometer (AA 7000-Shimadzu) and the elimination of lead efficiency was evaluated (Gouamid *et al.*, 2014; Mohammadi *et al.*, 2017).

According to the following equation was calculated the percentage of metal adsorption:

$$\text{Removal \%} = \{(C_i - C_e)/C_i\}*100$$

Where Ci and Ce are the initial and equilibrium concentration of metal ion (mg L^{-1}) in solution.

The adsorption capacity was determined by calculating the mass balance equation for the adsorbent

$$q_e = (C_i - C_e)\ V/W$$

Where q_e is the adsorption capacity (mgg^{-1}), V is the volume of the metal ion solution (L), and W is the weight of the adsorbent (g).

FT-IR measurements

The infrared spectroscopy (FT-IR) of the surface adsorbent was measured using a disk of potassium bromide; it was used (FT-IR-8400s type shimadzu) to characterize the active groups present on the surface of DPT using the wave number range of 200-4000 cm^{-1}.

SEM analysis

An analysis of scanning electron microscopy (SEM) was performed to examine the morphology of the adsorbent material. The samples were mounted on pieces of brass with double-sided tape. The SEM images were taken with a scanning electron microscope (TESCAN MERA III, Czech Republic) with several magnifications of × 800 - × 7500. The working distance of 4 to 5 mm was maintained and images were taken at an acceleration voltage of 25 kV for the leaf and the Blade and 50 kV for the Fiber using a secondary electron detector.

RESULTS AND DISCUSSION

Effect of contact time in the adsorption of lead by DPT

Triplicate experiments were carried out to detect the time needed for Pb adsorption by DPT Pinnae to achieve balance in time (0-90) min. 20 °C, pH 6.5, and 200 rpm. The results showed higher adsorption in 40 min which reached (0.6476 mgg^{-1}, 86.35%) and the equilibrium was at 50-90 min. In contrast, the higher adsorption of Pb by DPT Blade was in 20 min (0.6763 mgg^{-1}, 90.18%) and the equilibrium was at 60-90 min (Table 1). This is may be related to that the elimination of metal increasing rapidly in the first minutes because of the surface detected by the adsorbents and the dependence of the adsorption on the surface (Qadeer and Akhtar, 2005). Zadeh *et al*. (2014) achieved a maximum removal of Pb with a contact time of 40 minutes by *Ceratophyllum demersum*, while Keskinkan *et al.* (2004) found a maximum removal of Pb after 20 minutes.

Table 1. Adsorption of lead by DPT in different times

Time	Weight capacity of Adsorption mgg^{-1} (q_e)	Adsorption %
	Pinnae	
0	0.5876	78.35
5	0.6346	84.58
10	0.6365	84.87
20	0.6454	86.06
30	0.6472	86.29
40	**0.6476**	**86.35**
50	0.6475	86.33
60	0.6475	86.33
90	0.6475	86.33
	Blade	
0	0.5814	77.52
5	0.5659	75.45
10	0.6633	88.44
20	**0.6763**	**90.18**
30	0.6615	88.20
40	0.6711	89.49
50	0.6766	90.16
60	0.6768	90.17
90	0.6768	90.17
	Fiber	
0	0.5234	69.79
5	0.5778	77.05
10	0.5774	76.99
20	0.5774	76.99
30	**0.6031**	**80.42**
40	0.6021	80.28
50	0.6021	80.28
60	0.6006	80.08
90	0.4484	59.73

DPT Fiber adsorbed Pb in 30 minutes (0.6031mgg^{-1}, 80.42%) and the balance was 40-50 minutes. During 90 minutes, the speed of adsorption slowed down in later phases due to the reduction of sites, adsorbate transported from the external surface to the internal surface of absorbing particles. Many researchers (Dixit *et al.*, 2014; Thijar *et al.*, 2014 and Hasson, 2015) found that the contact time for removal of pb was 30 minutes. Other researchers (Hikmat *et al.*, 2014 and Soliman *et al.*, 2016) found that, with an increase in the contact time, removal of Pb from the aqueous so lution tested by activated carbonate, achieved an equilibrium status in three hours. The explanation for the researchers' similarities and differences may be the experimental conditions and the physiological differences of the plants used.

Effect of Temperature

The temperature is a crucial parameter in adsorption reactions by used the optimum time

Table 2. Adsorption of lead by DPT in different Temperature

Temperature °C	weight capacity of Adsorption mgg^{-1} (q_e)	Adsorption %
	Pinnae	
15	0.6544	87.25
25	0.6483	86.44
35	0.6241	84.55
45	0.6330	85.74
55	0.6454	86.03
	Blade	
15	**0.6761**	**90.15**
25	0.6624	88.32
35	0.6595	87.94
45	0.6407	86.77
55	0.6643	88.58
	Fiber	
15	0.4166	55.55
25	**0.5477**	**73.03**
35	0.4636	61.82
45	0.5459	72.79
55	0.5212	69.49

condition of the last experiment for all the DPT, (15-55) °C, pH 6.5, and 200 rpm. The results of the present study showed higher adsorption in 15°C for each Pinnae and Blade (0.6544mgg^{-1}, 87.25%), (0.6761mgg^{-1}, 90.15%) respectively, and higher adsorption was in 25 °C for DPT Fiber (0.5477mgg^{-1}, 73.03%) (Table 2). Other researchers (Al-Haidary *et al.*, 2011 and Samra *et al.*, 2014) found that the effective temperature degree for removal Pb was 25 °C. As is known, the adsorption process is decreasing with the temperature increasing, and molecules previously adsorbed on a surface tend to desorb from the surface at a high-level temperatures. In addition to that, this phenomenon may be lead to weak adsorption interaction between biomass surface and metal ions that support physi-sorption (Vinod and Anirudhan, 2001 and Horsfall and Spiff, 2005).

Effect of pH

The acidity of the solution (pH) is one of the most significant components for the adsorption of heavy metals from wastewater and aqueous solutions. The optimum time and temperature of the last experiment results from the DPT was used in this study, pH (4.5-8.5), and 200 rpm. The results of the adsorption of lead was 0.6561mgg^{-1} (87.48%) for Pinnae and 0.6668 mgg^{-1}(88.91%) for Blade at the pH 6.5 then decreasing with the increasing of pH (Table 3). These results accordance with Haleem and Abdulgafoor (2010) who observed that, the maximum biosorption was obtained at pH 7. Surface adsorption is a physicochemical phenomena and, because the cell walls are multi-plant, it may bind Heavy Metals (amine, carboxyl, sulfhydryl, phosphate and thiol), through their functional classes. These groups have various affinities and characteristics for metal bonding (Lui *et al.*, 2006).

Meanwhile, the adsorption of Pb by DPT Fiber increases significantly to 0.6795 mgg^{-1} (90.60%) at pH 5.5 (Table 3). Conversely, many researchers (Al-Haidary *et al.*, 2011; Boudrahem *et al.*, 2011 and Ghorbani *et al.*, 2012) observed that, the solution at acidic pH has a good adsorption capacity. The elimination efficiency was high due to the protonation of the active sites and at an increasing charge density at the surface of the adsorbent (phenolic, carboxylic and hydroxyl) (Ngah and Hanafiah, 2008).

Effect of Mixing Speed

From Table 4 the maximum adsorption was 0.6558mgg^{-1} (87.44%) at100 rpm for Pinnae and 0.6769mgg^{-1} (90.26%) for Blade, whereas the maximum absorption for Fiber was 0.5420mgg^{-1} (72.27%) at 50 rpm by used the optimum (Time, Temperature and pH) condition result for all the DPT in this study and (50-200) rpm. While Singh and Zahra (2014) found that, the optimal mixing speed for the solution- Emblica officinal is Pinnae powder mixture is approximately 170 rpm.

Table 3. Adsorption of lead by DPT in different PH

pH	weight capacity of Adsorption mgg^{-1} (q_e)	Adsorption %
	Pinnae	
4.5	0.2515	33.53
5.5	0.4761	63.49
6.5	**0.6561**	**87.48**
7.5	0.0385	5.13
8.5	0.2177	29.03
	Blade	
4.5	0.6186	82.48
5.5	0.6452	86.03
6.5	**0.6668**	**88.91**
7.5	0.4948	65.97
8.5	0.5557	74.09
	Fiber	
4.5	0.6086	81.15
5.5	**0.6795**	**90.60**
6.5	0.5860	78.13
7.5	0.6484	86.46
8.5	0.6476	86.35

Table 4. Adsorption of lead by DPT in different Mixing Speed.

Mixing Speed (rpm)	weight capacity of Adsorption mgg^{-1} (q_e)	Adsorption %
	Pinnae	
50	0.6515	86.87
100	**0.6558**	**87.44**
150	0.6561	87.43
200	0.6482	86.42
	Blade	
50	0.6668	88.91
100	**0.6769**	**90.26**
150	0.6737	89.83
200	0.6622	88.30
	Fiber	
50	**0.5420**	**72.27**
100	0.5199	69.32
150	0.4491	59.88
200	0.5150	68.677
	FT-IR	

It is clear that the increase in agitation speed only contributes to a certain limit in the adsorption process, which elsewhere does not increase the adsorption potential significantly. (Shiau, and Pan, 2004; Ihsanullah *et al.,* 2015). However, may occur the opposite in some cases, the higher agitation speed lead to a decrease in the capacity of adsorption (Jamil *et al.,* 2011; Omri *et al.,* 2012). The kinetic energy of the adsorbed molecules and the adsorbent particles increased enough to collide rapidly with each other, leading to a detachment of the loosely bound adsorbed molecules, as Jamil *et al.,* (2011) suggested.

FT-IR

The FT-IR spectroscopy is an important spectrometer of characterizing different active groups. Figure 1 represents the infrared spectrum of the Pinnae powder at a range of 200-4000 cm^{-1}. The infrared spectra showed a strong beam at 3340 cm^{-1}, which is due to the hydroxyl group OH while the C-H group appeared at 2920 and 2854 cm^{-1}. Also, a carbonyl group band was found at 1732 cm^{-1} while the band at 1647 cm^{-1} may be attributed to the C = C and C = N group, which is included in the cellulose composition, whereas the C-O and C-N bands were shown at 1234 and 1357 cm^{-1}.

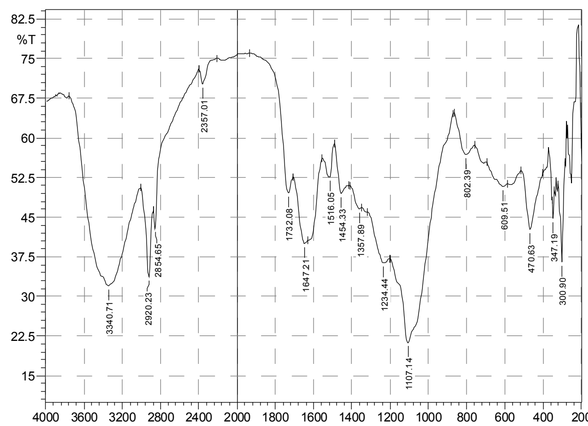

Fig. 1. FTIR spectra of DPT pinnae before pb adsorption

The infrared spectra of the Blade (Fig. 2) shows a variety of bands indicating that there are several active groups responsible for the adsorption of the elements. The hydroxyl groups (OH) showed at the wave number 3340 cm^{-1}, which are inserted into the cellulose structure, because the glucose unit structure of cellulose the appearance at 1735 cm^{-1}, which is due to the presence of a carbonyl group (C = O) additionally to the presence of the group C = C and C = N, which appeared at 1624 cm^{-1}, and the C-O and C-N groups showed at 1253 cm^{-1} and 1350 cm^{-1}, respectively. All these groups have the ability to bind lead in the different processes as physical or chemical adsorption.

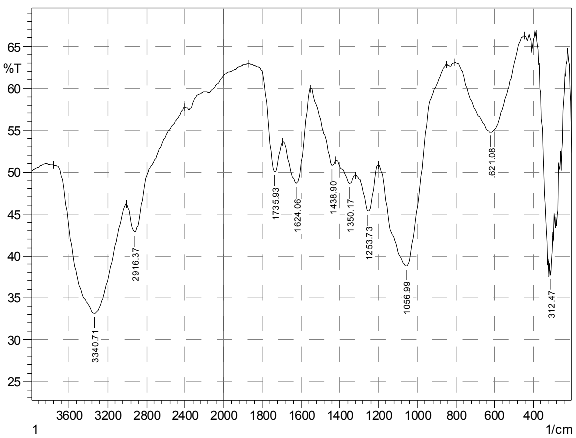

Fig. 2. FTIR spectra of DPT blade before pb adsorption

In the palm, Fiber powder (Fig. 3) the hydroxyl group is shown at the wave number 3415 cm^{-1} and the appearance of the C-H group at 3924 cm^{-1}. The carbonyl group C = O appeared at 1732 cm^{-1} and the band of C = C and C = N at 1635 cm^{-1}. The polar groups with single bonds such as C-O and C-N appeared at 1247 cm^{-1} and 1370 cm^{-1}. The functional group (C = O) at 1732 cm^{-1}, O-H at 3400 cm^{-1} and C-H at 2853 cm^{-1} was also found in the date palm Fiber of Amin *et al.,* (2016). The availability of hydroxyl groups on the surface of the adsorbents has improved Chemi-sorption. The changes in the vibrational frequencies (band intensity for the whole range) confirm the formation of new links among functional groups on the adsorbent surface and in solution adsorbate (Gebrehawaria *et al.,* 2015).

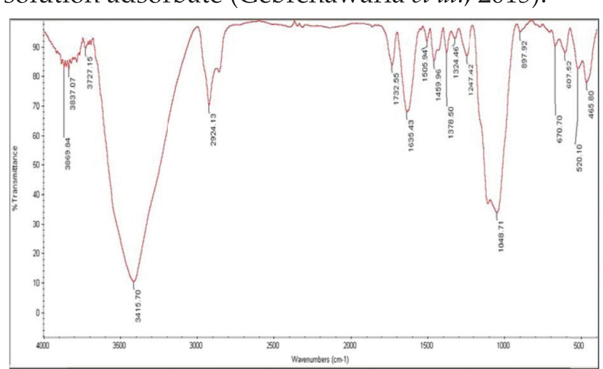

Fig. 3. FTIR spectra of DPT fiber before Pb adsorption

SEM

The images showed asymmetric pores that were raw on the surface of DPT before Pb absorption (Fig.

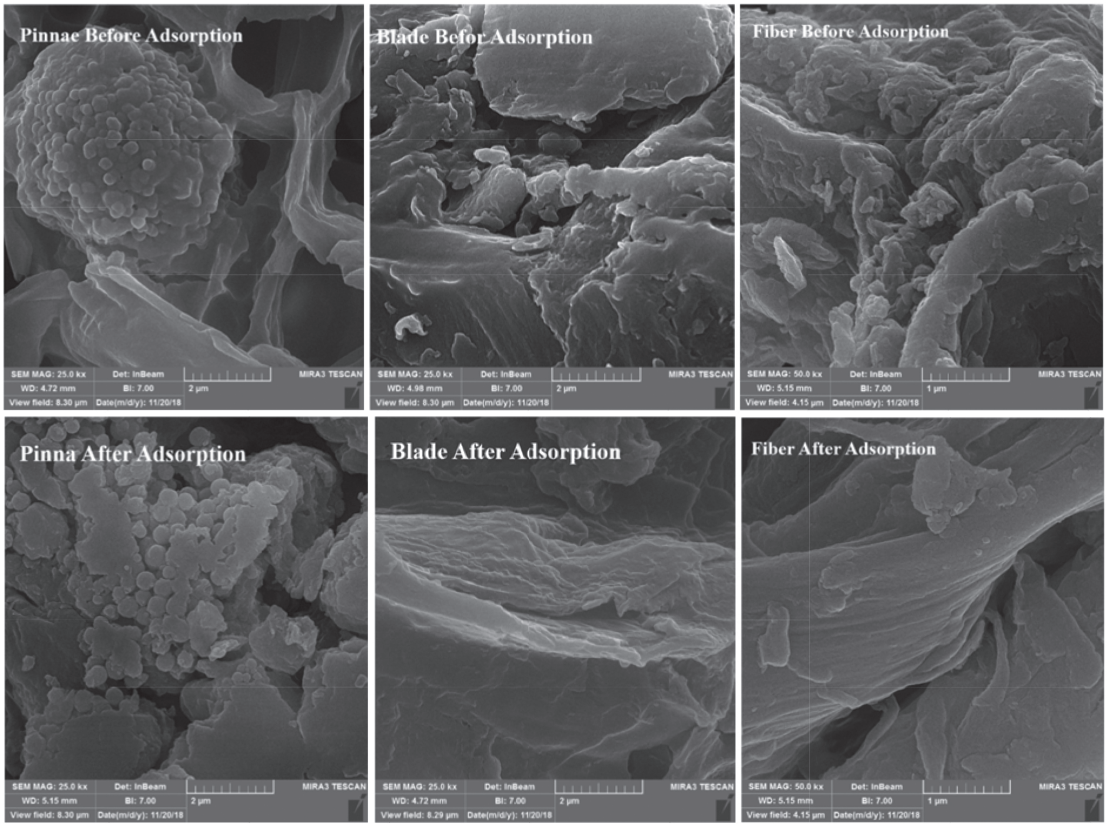

Fig. 4. SEM photographs of DPT before and after Pb adsorption

4). These canals seem to consist of lignin-connected multicellular fibers. The raw surface of the DPT will increase the interaction with the Pb metal ions. The central vacuum in the DPT can also be observed. After the Pb absorption, the surface of a DPT with closed pores is very fluid and bright due to the physicochemical interaction between the contaminant and the functional groups on the DPT Fiber surface. The structural alteration of the surface of the DPT can be correlated with the impact of the metal ions.

Application the optimum conditions in industrial sample

The industrial sample has brought from the waste of Nahran Umar field, western of Basra, Iraq. The optimum conditions (pH, time, temperature and mixing speed) which applied in the water solutions have been applied in this experiment and the results were shown in Table 5.

The adsorption of lead was (0.2837mgg^{-1}, 37.68%), (0.3278mgg^{-1}, 41.11%) and (0.3934mgg^{-1}, 49.71%) by Pinnae, Blade and Fiber respectively. The percentage of lead elimination in the real sample was lower than the aqueous solutions, maybe because of the real sample contained a crude oil, which led to the overlap of another factor to compete for binding to the active sites of the adsorbent surface with a lead. Ahmed (2012) also found that the wastewater produced by the petroleum industry and the processing of crude oil characterized by high levels of crude oil products

Table 5. Adsorption of lead in the industrial sample by DPT

Adsorbent	Time (min)	pH	Temperature °C	Mixing speed	Weight capacity of Adsorption mgg^{-1} (q_e)	Adsorption %
Pinnae	40	6.5	15	100	0.2837	37.68
Blade	20	6.5	15	100	0.3278	41.11
Fiber	30	5.5	25	50	0.3934	49.71

and other product chemicals. The effect of a different pollutant concentration if the coexisting pollutant competes or forms a complex with a target contaminant for the binding sites, a higher concentration of another pollutant will reduce the biosorption removal of the target pollutant (Abdi and Kazemi, 2015).

Most studies indicate that, because of their chemical structure, the removal potential of heavy metal ions from DP residues is greater than other natural waste. DP Fibers are lignocellulose compounds made up of three essential components: cellulose (40-5%), hemicellulose (20-35%) and lignin (15-35%) (Al-Kabbi et al., 2005). Lignin is the most significant component and has complex chemical components within the DP waste material, since it is a three-dimensional polymer of C-C or C-O-C bound phenyl propane units. The elementary composition therefore has a high carbon (62% by weight) and a lower oxygen (32% by weight). A higher number of carbon atoms typically are related to a lower polarity and hence a greater absorption potential and lignin is very influential on the absorption process due to its large number of carbon atoms. For this reason, the ideal adsorbent for absorption techniques is a lignocellulosic material (Barreveld, 1993).

CONCLUSION

DPT is a renewable, economical and environmentally friendly material which is available in large amounts and disposed of in countries where it is cultivated as waste after annual cultivation. DPT filters may be a possible commercial technology for the removal from industrial wastewater of heavy metals and other pollutants.

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