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To cite this article: Ming Zhang, Li Heng Xu, Sang Soo Lee & Yong Sik Ok (2016) Sorption of polycyclic aromatic hydrocarbons (PAHs) by dietary fiber extracted from wheat bran, Chemical Speciation & Bioavailability, 28:1-4, 13-17, DOI: [10.1080/09542299.2015.1136569](https://doi.org/10.1080/09542299.2015.1136569)

To link to this article: <https://doi.org/10.1080/09542299.2015.1136569>



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Published online: 01 Feb 2016.



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Sorption of polycyclic aromatic hydrocarbons (PAHs) by dietary fiber extracted from wheat bran

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ABSTRACT

The unintentional ingestion of carcinogenic xenobiotic substances leads to the high risk of cancer. Dietary fiber (DF) may protect against cancer by sorbing such chemicals. To this end, the sorption of four polycyclic aromatic hydrocarbons (PAHs) to DF extracted from wheat bran (WB) was studied. The strong affinity of PAHs to DF and WB indicated the effective binding of PAHs, and their distribution coefficients (K_d) positively increased with the increase in hydrophobicity of the PAHs. The DF had much higher K_d values for all PAHs compared to those of the unprocessed WB. The DF extraction process removed hydrophilic residues, such as starch, from WB, and increased the roughness of DF surface. Loss of hydrophilic components from WB to DF led to much higher affinity of DF with PAHs than WB. The results indicate that the DF can effectively sorb and remove xenobiotics, thereby having the potential to lower carcinogenic risk to humans.

ARTICLE HISTORY

Received 1 October 2015
Accepted 23 December 2015

KEYWORDS

Adsorption; emerging contaminant; human health; food waste; sorption isotherm

Introduction

In recent decades, the increases in chemicals utilization and waste emission worldwide have led to the frequent occurrence of xenobiotic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), in soil, water, and air environments.[1–3] The unintentional ingestion of these chemicals via food and water leads to their accumulation and magnification in the human body, thereby potentially threatening human health.[4]

A high intake of dietary fiber (DF) has been correlated to a decrease in colon cancer, and both epidemiologic studies and meta-analyses reviewed by Trock et al. [5] revealed a protective effect against human colon cancer of fiber-rich diets. The protective mechanisms were previously proposed for DF against colon cancer. For example, Stephen and Cummings [6] suggested that DF in diet may increase fecal weight and decrease transit time, thereby reducing the interaction of carcinogens with colonic mucosa. Some DFs can be readily degraded by bacteria in the colon and can be fermented to short-chain fatty acids (SCFAs) that can inhibit the conversion of bile acids to effective tumor promoters.[7–10] Furthermore, SCFAs, especially butyrate, can induce differentiation or apoptosis of cells that may otherwise progress to malignant transformation.[9, 11] Direct removals of mutagens and carcinogens by DFs were also observed,[12–14] which were expected to carry xenobiotic chemicals out of the

body via feces and consequently lower the effective concentration of mutagenic and carcinogenic chemicals in the alimentary tract.

However, the sorption of these chemicals to the DF varied depending on the properties of both the chemicals and the DF. For example, Harris et al. [14] found that the increase in hydrophobicity of 6 heterocyclic aromatic amines increased their ability to adsorb onto model DFs. Ferguson et al. [12] concluded that DF from monocotyledons, mainly cell wall, had a much higher sorption capacity than that from dicotyledons.

Therefore, a better understanding of the removal of different xenobiotics by DF derived from different diets is required. This study investigated the *in vitro* sorption of four PAHs to DF extracted from wheat bran (WB). The results of this study are expected to support the protective effect of DF on human health via sorption of these xenobiotics.

Materials and methods

Cereal brans are usually selected as good sources of DF, which is mainly in the form of cell walls. WB contains the DF typically less than 40–50%,[9] and is considered to be one of the most important source of DF for humans. Therefore, WB was selected as the raw material to extract DF used in this study. The extraction process followed the combined enzyme–chemical extraction

method described by Zheng [15]. Briefly, the WB was washed with de-ionized water for 30 min, dried at 55 °C overnight, ground and then passed through a 50-mesh sieve as the raw WB for further use. Approximately 10 g of raw WB was mixed with 100 mL of water, and then the mixture was heated in a water bath at 65 °C for 20 min. Enzymolysis in a 120-mL solution containing 1 g of α -amylase (>3700 U/g) and 4 g of saccharifying enzyme (>100,000 U/g) was then performed at 65 °C for 100 min. The enzymes were deactivated at 100 °C for 10 min, and then hydrolysis in 5% NaOH solution was performed at 60 °C for 70 min. Next, the residue was filtered and washed to neutral with water and was dried at 105 °C to achieve a constant weight. The final product was considered to be the DF. The morphology of the WB and the DF was characterized using a scanning electron microscopy (SEM, HITACHI SU8010).

Naphthalene (Naph), acenaphthene (Ace), phenanthrene (Phen) and pyrene (Pyr) were selected as model hydrophobic contaminants in this study. All of them was purchased from J&K Chemical with >98% purity. Sorption isotherms were studied using batch sorption techniques at 37 °C to mimic the human body temperature. Stock solutions of four PAHs were separately prepared with concentrations below their water solubility, and these solutions were then diluted to series concentrations for the isotherm study. All solutions contained 0.02-mol/L NaCl to maintain ion strength and 0.02% NaN_3 to avoid any possible biodegradation. To provide a controllable aqueous condition, no additional digestive juice was added. Different amounts of WB and DF were used for sorption experiment to achieve a removal rate for PAHs of 30–70% to accurately determine the isotherms. All tubes were sealed with a Teflon-lined screw cap, shaken in a shaker for 24 h, and then centrifuged at 3000 rpm for 10 min.

After centrifugation, 5 mL of supernatant was transferred to a 10-mL colorimetric tube and then was mixed with a high performance liquid chromatography (HPLC) grade methanol to a total volume of 10 mL to avoid possible loss during the analysis. The samples were analyzed using a Agilent 1260 HPLC equipped with a 4.6×150 mm reverse phase C18 column and a fluorescence detector using methanol and water mixture (90:10, V:V) as mobile phase. The excitation wavelength of Naph, Ace, Phen and Pyr are 220, 225, 244 and 270 nm, respectively, while their emission wavelength are 310, 315, 360 and 380 nm, respectively. Each treatment was prepared in duplicate, and the control samples were prepared accordingly to account for possible losses due to volatilization or adsorption onto the tubes. The amount of PAHs sorbed to WB or DF was calculated as the concentration differences between the control samples and the samples with WB or DF according to Equation (1). [16,17]

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

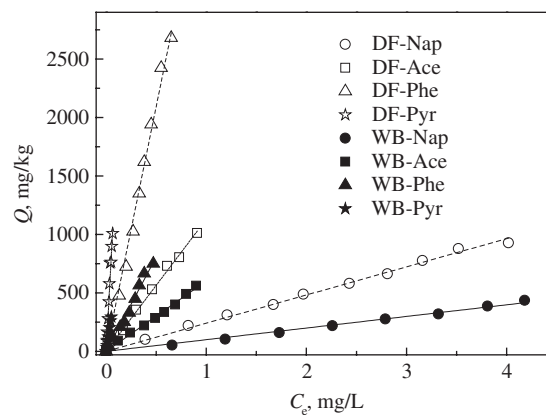


Figure 1. Sorption isotherms of naphthalene (Nap), acenaphthene (Ace), phenanthrene (Phe) and pyrene (Pyr) on dietary fiber (DF, hollow dots) and wheat bran (WB, solid dots). Q (mg/kg) is the sorption amount of polycyclic aromatic hydrocarbons (PAHs) on DF or WB at equilibrium concentration of PAHs (C_e , mg/L).

Table 1. Distribution coefficients (K_d) of polycyclic aromatic hydrocarbons (PAHs) between dietary fiber (DF)/water and wheat bran (WB)/water.

Chemicals	Dietary fiber		Wheat bran	
	K_d	r^2	K_d	r^2
Naphthalene	241	0.9987	99.5	0.9977
Acenaphthene	1130	0.9987	602.4	0.9982
Phenanthrene	4198	0.9946	1608	0.9884
Pyrene	15970	0.9779	5794	0.9958

where q_e is the equilibrium sorption amount of PAHs on DF or WB at their equilibrium concentration C_e .

Results and discussion

All of the sorption isotherms for four PAHs by DF and WB were studied through a batch sorption experiment, and the results are shown in Figure 1. Apparently, all the isotherms were highly linear with R^2 values greater than 0.97, and the majority of which having values greater than 0.99, (Table 1) indicating a partitioning-dominated mechanism during sorption. [18] The DF mainly consists of plant cell walls, and the structure and composition of DF varies depending on plant species. [9] In general, the main compositions of DF include polysaccharides (e.g. cellulose and hemicellulose), phenolic components (e.g. lignin and suberin), lipids (e.g. cutins and waxes) as well as some proteins and inorganic components. [9] As a feedstock of DF, the WB contains more carbohydrates after wheat processing, such as residue starch, which was mostly removed through extraction using the artificial digestion extraction as mentioned above.

Jonker [19] observed the linear sorption of 13 PAHs by cellulose and found that even large molecules of PAHs can penetrate into amorphous domains within the cellulose at equilibrium. In our previous study, Zhang et al. [20] also revealed that the sorption of three PAHs by

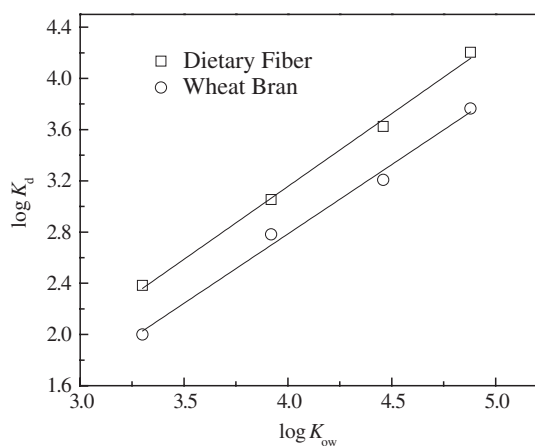


Figure 2. Relationship between hydrophobicity of polycyclic aromatic hydrocarbons (PAHs) indexed by log octanol–water partition coefficients ($\log K_{ow}$) and log distribution coefficients ($\log K_d$) of PAHs between dietary fiber (DF)/water and wheat bran (WB)/water interface.

lignin was governed by hydrophobic partitioning into the abundant amorphous structure of lignin for PAHs sorption. Lipids, although with minor weight fraction in plant, are the predominant components in plant for the partitioning of hydrophobic contaminants such as PAHs due to their lipophilic nature.[18] Consequently, as an aggregation of the above-mentioned components, sorption of PAHs by DF and WB was mainly governed by the partitioning process, and linear sorption isotherms were apparently observed.

Due to the linear characteristics of all sorption isotherms, the distribution coefficients (K_d) of all PAHs on DF and WB can be obtained using a linear regression as described in Equation (2):

$$Q = K_d C_e \quad (2)$$

where Q is the sorption amount of PAHs on DF or WB at the equilibrium concentration (C_e), and K_d is the distribution coefficient.

The K_d values of four PAHs were summarized in Table 1, which was ranged from 241.0 to 15970 for the DF and from 99.5 to 5794 for the WB. The huge discrepancy among PAHs' K_d values was caused by their various hydrophobicity. As shown in Figure 2, the K_d values for the PAHs increased with the increase of their corresponding octanol-water partition coefficients (K_{ow}). Higher K_{ow} values showed higher hydrophobicity, indicating a positive correlation between the K_d values and the hydrophobicity of the PAHs. The linear regressions between the $\log K_d$ of both DF and WB and the $\log K_{ow}$ of the four PAHs suggest a hydrophobicity-driven sorption process.

The values of K_d describe the migration behavior of the PAHs between DFs and aqueous solution, which indicates the capability of DF to remove xenobiotics. Higher K_d values indicate a higher removal efficiency. In this study, the removal efficiency of DF on PAHs followed the order of Nap < Ace < Phe < Pyr.

However, due to the unavailability of the K_d , it is difficult to estimate the possible removal rate of a certain chemical. As a result, the relationship between the K_d values and the available parameters of chemicals, such as K_{ow} , is required for predicting the unavailable K_d data. Based on the observed data in this study, the relationships between K_d and K_{ow} were established, and these relationships can be expressed as follows:

$$\log K_{d-DF} = 1.14 \log K_{ow} - 1.39 \quad (3)$$

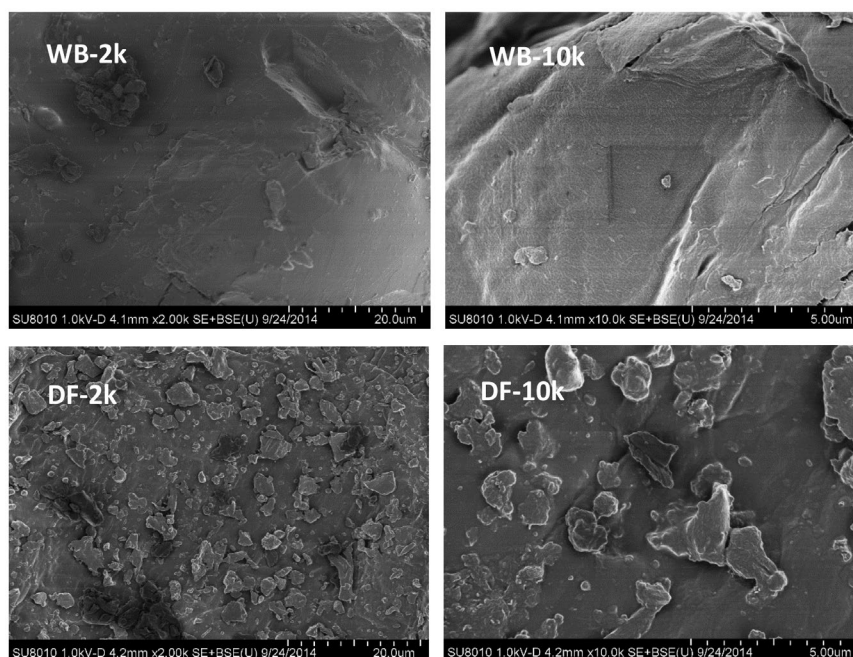


Figure 3. Scanning electronic microscopy (SEM) images of wheat bran (WB) and dietary fiber (DF). WB-2k and WB-10k stood for WB at scale of 2000 \times and 10,000 \times magnification, while DF-2k and DF-10k stood for DF at scales of 2000 \times and 10,000 \times magnification, respectively.

$$\log K_{d-WB} = 1.08 \log K_{ow} - 1.55 \quad (4)$$

These equations can be used to estimate the K_d values of PAH or possibly other nonionic hydrophobic organics based on their corresponding K_{ow} values. However, more experimental data are required to obtain a more accurate equation for the K_d estimation of different types of organic contaminants.

The slopes for both equations were close to 1.1, which means that the K_d values for both DF and WB increased with a similar trend as a function of PAHs' hydrophobicity. However, it can be concluded from Equations (3) to (4), as well as Table 1 and Figure 1, that the K_d values of WB were significantly lower than those of DF. The K_{d-DF} values of the tested PAHs were approximately twice that of K_{d-WB} , indicating a better sorption capability of DF against WB. One of the reasons is that the DF had a better sorption capability than the WB, possibly resulting from the extraction process of DF. The hydrophilic residues, such as starch from the WB, have an extremely weak affinity with PAHs [21] and were removed during extraction; thus, the sorption of the PAHs by an unit weight of the DF increased relative to that of the WB.

In addition, SEM was employed to observe the differences in the morphologies of DF and WB. Both 2000 \times and 10,000 \times magnification of DF and WB are presented, which are shown in Figure 3. It showed that there is almost no pore structure in both DF and WB, and their surface area should be very low since the Brunauer–Emmett–Teller (BET) surface area of DF and WB cannot exactly measured and was not presented in this study. This indicated that strong sorption of PAHs onto DF and WB was probably not governed by surface adsorption and the partitioning of PAHs into biomass may be the key process. Furthermore, lots of embossments were observed on the DF rather than the WB due to components degradation and removal by enzymolysis and hydrolysis during the DF extraction. The embossments on the DF surface increased the roughness of DF compared to that of WB, which may provide higher accessibility of PAHs onto the DF. However, because the sorption of PAHs on DF and WB was governed by partitioning process, the differences of sorption capability between DF and WB were caused by the components difference.

Conclusion

In this study, the removal of four PAHs by DF via sorption exhibited a very high efficiency because the K_d values between DF and water were very high, ranging from 241 to 15,970. The relationship between K_d and K_{ow} was established. Loss of hydrophilic components, such as starch, led to a higher sorption capacity of the DF than the WB towards hydrophobic organics, such as PAHs. However, due to the complexity of the aqueous environment in the alimentary tract, the distribution behavior of xenobiotics between DF and digestion juice may

be varied. Nevertheless, the higher sorption capability nature of DF provided evidence that the use of DF can effectively sorb and remove xenobiotics, thereby potentially lowering carcinogenic risk.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was financially supported by the Natural Science Foundation of Zhejiang Province [grant number LQ12B07003] and the National Natural Science Foundation of China [grant number 21307122].

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