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RESEARCH ARTICLE

SAFOU (*DACRYODES EDULIS*) SEEDS APPLIED TO THE REMOVAL OF BISPHENOL A IN SOLUTION. IMPLICATION OF SURFACE ANTIOXIDANT MOLECULES ON THE CHEMICAL SORPTION OF THE ENDOCRINE DISRUPTOR

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ABSTRACT

In this study, the fine fraction (< 100 µm) of safou seeds (*Dacryodes edulis*) was characterized and then applied to the removal of bisphenol A (BPA) form aqueous solution. The techniques used include scanning electron microscopy (SEM) which allowed access to the morphology of the material, Fourier transform infrared (FTIR) spectroscopy which revealed the chemical functions on its surface and BET technique from which its specific surface area was determined. Its behavior towards BPA was studied in batch mode under the effect of the variation of several parameters among which the contact time, the equilibrium pH, the adsorbent dosage and the adsorbate initial concentration. The optimal contact time and BPA adsorption pH were 25 min and pH 3, respectively. The pseudo-second order kinetic model and the Freundlich isotherm better fit the adsorption of BPA on safou seeds. The maximum adsorption capacity was 24.5 mg.g-1 obtained experimentally. The surface molecules of safou seeds, consisting predominantly of antioxidants (phenols, flavonoids, vitamin C) and fatty acids (palmitic, oleic and linoleic acid), effectively contribute to the chemical sorption of BPA by the formation of covalent bonds and hydrogen bonding. With so many functional molecules on its surface, safou seeds could be applied to the treatment of water containing bisphenol A.

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INTRODUCTION

Bisphenol A (BPA), which is very involved in the manufacture of most common objects (banknotes, receipts, toys, baby bottles, dental appliances, etc.), is now perceived as a modifier of endocrine function (European Union, 2000). For this reason, the use of BPA in food contact materials is banned in France, and based on a highly precautionary approach**,** the production and sale of BPA-based polycarbonate baby bottles is no longer permitted under European law (Christensen *et al.,* 2014). The sources of BPA are diverse, with the main ones being user industries and municipalities (Birkett and Lester, 2003; Flint *et al.,* 2012). Bisphenol A, found in tap water, surface water, air and foodstuffs in considerable quantities (Ballesteros-Gómez *et al.,* 2009; Arnold *et al.,* 2013), is now part of the so-called emerging pollutants, which is feared for its mutagenicity, carcinogenicity (Kery *et al.,* 2007; Izotti *et al.,* 2009) and adverse effects on the vital organs (Colerangle and Roy, 1997; Bindhumol *et al.,* 2003). To overcome this, it would be necessary to act upstream by treating wastewaters which convey BPA before rejection in the receiving medium. For this, several processes have already been used, with more or less satisfactory results (Zhang *et al.,* 2006; Rachael *et al.,* 2012). In a recent study, we showed that the soft and white part of orange peel (albedo) was able to absorb BPA better than some activated carbons (Kamgaing *et al.,* 2017a). Thus, agricultural and industrial residues considered as waste resources could contribute effectively and at a reasonable cost to the elimination of certain endocrine disruptors in water. The seeds of safou (*Dacryodes edulis*) are part of the waste resources. However, they are rich in saturated fatty acids (mostly palmitic acid), unsaturated fatty acids (oleic and linoleic acids) and antioxidants (Ajayi and Adesanwo, 2009; Ogunmoyole *et al.,* 2012). These surface molecules could contribute effectively to the chemisorption of BPA. In this study, dried and sprayed seeds of *Dacryodes edulis* are characterized before being applied to the removal of BPA in aqueous solution.

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MATERIALS AND METHODS

Preparation and characterization of the biosorbent

Adsorbent from safou seeds

Safou fruits (Figure 1) were purchased from the Dschang Market, Cameroon. Once washed, they were opened to obtain the seeds which were subsequently dried under the sun. The dried seeds were pulverized by a mill and sieved. Fine particles with a diameter less than 100 microns (hereafter designated DAS) were put in polystyrene bags and stored at room temperature until further use.

All the chemicals used throughout this study were analytical grade reagents. All adsorption experiments were performed in sealed 50 mL glass conical bottles that contained 40 mg of DAS and 15 mL of a BPA solution in the appropriate concentration. An adsorption kinetic study was carried out with an initial BPA concentration of 60 mg.L^{-1} at room temperature, pH 6, and a constant mass of DAS (40 mg). The mixture was stirred at 200 rpm and at different time intervals from 3 to 30 min. After adsorption experiments, the suspensions were filtered through 0.45 µm membrane filters. The concentration of BPA was assayed using a UV-Vis spectrophotometry, Jenway 6715, at 279 nm.

(a) (b) (c)

Figure 1. Photograph of safou (*Dacryodes edulis*): (a) fruits, (b) dried seeds, (c) powdered safou seeds

Table 1. Characteristic properties of DAS

Surface area (m^2.g^{-1})	Equilibrium pH (pH$_{eq}$)	pH$_{PZC}$	Bulk density (g.cm^{-3})	Moisture content (%)	Dry matter content (%)
0.69	6.95	5.85	0.40	9.76	90.24

Characterization of the adsorbent

The Brunauer−Emmett−Teller (BET) specific surface area of the samples was characterized by nitrogen adsorption at 77 K with a Micromeritics instrument, Gemini Model 2380. Energy dispersive X-ray spectroscopy (EDX) helped to determine the elementary composition of *Dacryodes edulis* seeds. Scanning Electron Microscopy (Phillips XL 30, Netherlands) images were taken to know the surface morphology of the samples. Fourier transform infrared (FTIR) spectra were recorded on a FTIR Bruker Alpha-P spectrophotometer between 4000 and 400 cm^{-1} using KBr pellets. The point of zero charge (pH$_{pzc}$) was determined following the procedure given by Lopez-Ramon (Lopez-Ramon *et al.,* 1999).

Batch adsorption experiments

BPA ($(CH_3)_2C(C_6H_4OH)_2$, molecular weight 228.29) is poorly soluble in water, soluble in ethanol and stable in hydrogen peroxide medium. For this reason, the stock solution of BPA (250 mL, 1 g.L^{-1}) was obtained by dissolving a known amount of this compound in ethanol and hydrogen peroxide solution (30% v/v, 10% v/v respectively). Different concentrations ranging from 15 to 70 mg.L^{-1} of BPA were then prepared from the stock solution. The effect of pH on the adsorption of BPA was studied with 15 mL of BPA (60 mg.L^{-1}) and 40 mg of DAS in a pH range from 2.0 - 11.0 at room temperature (297.4 K). The solution pH was adjusted with a 0.01 M HCl or NaOH solution.

RESULTS AND DISCUSSION

Characterization of *Dacryodes edulis* seeds (DAS)

Table 1 shows, among other properties, the specific surface area of the adsorbent. It appears that the BET surface area of DAS is less than 1 and similar to that of orange flavedo (Kamgaing *et al.* 2017b) and that of sawdust but significantly greater than that of rice husk (Yambo *et al.* 2012). The pH of zero charge (pH$_{pzc}$) of DAS is 5.85 (Table 1). This is the pH at which the overall charge of the material is zero. This is an important parameter for elucidating the adsorption mechanism. Thus, when the equilibrium pH (pH$_{eq}$) is higher than pH$_{pzc}$ as is the case, the surface of the material is negatively charged, a situation favorable to the adsorption of cationic adsorbates. Conversely, if pH$_{eq}$ < pH$_{pzc}$ the surface charge is positive and the adsorption of anionic adsorbates is favored. The morphological structure of DAS was characterized by SEM and is shown in Figure 2.The SEM image clearly exhibits the irregular nature of the surface of the biomaterial, pores being heterogeneous. This situation favors adsorption.

The bulk composition of DAS was investigated by energy dispersive X-ray (EDX) measurements. The EDX spectrum obtained is shown in Figure 3. The atomic and weight percentages of the biosorbent are summarized in Table 2, with carbon and oxygen being the most abundant elements by weight.

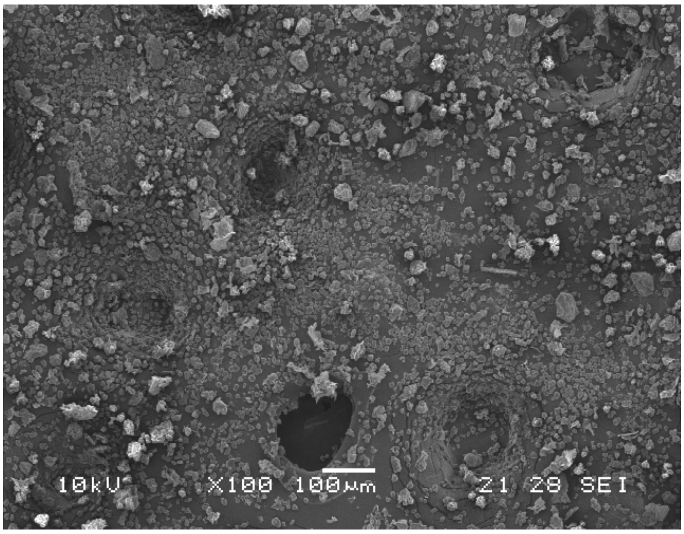


Figure 2. SEM micrograph of DAS

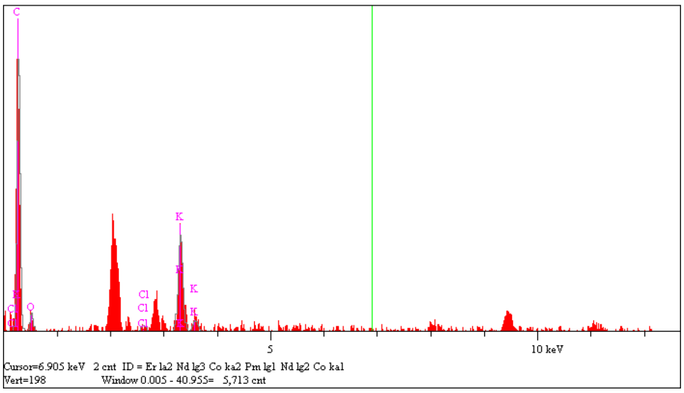


Figure 3. EDX spectrum of DAS

Table 2. Elemental analysis of DAS

Element	wt%	At%
K	4.766	13.307
O	15.782	18.032
C	79.146	67.887
Cl	0.306	0.775

FTIR spectroscopy is a helpful tool in identifying the presence of certain functional groups on the surface of materials. The FTIR spectrum obtained in the 4000 - 400 cm^{-1} spectral region is shown in Figure 4 and the band assignments summarized in Table 3. The peak at 3304.72 cm^{-1} can be attributed to the stretching vibration of O−H groups (polysaccharides, lignin, alcohols and phenols). The peaks at 2921.94 and 2852.67 correspond to C-H and CH_2 bond vibrations. The peak at 1708.87 cm^{-1} was assigned to C=O bonds in carboxylic acid and carbonyl moieties (saturated and unsaturated fatty acids). The peak at 1649.83 cm^{-1} was associated with the skeletal vibration of aromatic C=C bonds. The peak at about 1336.39 cm^{-1} corresponds to carboxyl O=C−O bonds (saturated and unsaturated fatty acids). The peak between 1336 and 997 cm^{-1} is assigned to epoxy C−O−C bonds (antioxidants flavonoids and vitamin C). The strong peak at 997 cm^{-1} can be attributed to the stretching vibration of C-H groups of aromatic polynuclear systems.

BPA adsorption kinetics

In many cases, the adsorbent rapidly fixes the adsorbate at the beginning of the adsorption process, its pores being completely free. As the pores are occupied, the process is slowed down to equilibrium, diffusion becoming the limiting factor for adsorption. Figure 5 illustrates this phenomenon. The first three minutes are marked by a rapid adsorption of BPA (increase of the adsorption capacity). After this time, the adsorption proceeds slowly until equilibrium for a total duration of 20 min. The contact time for subsequent experiments is 25 min, at the end of which the equilibrium is reached.

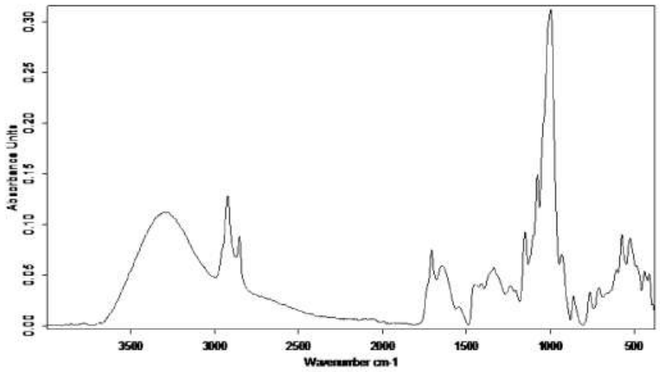


Figure 4. FTIR spectrum of DAS

Table 3. Characteristic infrared bands of DAS

Wave number (cm^{-1})	Assignment
3304.72	ν(O-H) polysaccharide, lignin, alcohols, phenols)
2921.94 and 2852.67	ν (C-H) aliphatic CH and CH_2
1708.87	ν(C=O) carboxyl in carboxylic acid and carbonyl moieties
1649.83	ν(C=C) aromatic bonds
1336.39	ν(O=C−O) carboxyl bonds
997.00	ν(C-H) aromatic polynuclear systems
572.45 and 522.55	ν(C-Cl)
1336-997	ν (C-O-C) epoxy bond

The adsorption capacity of DAS for BPA was calculated according to the equation 1 where C_0 and C_E represent the initial and equilibrium concentrations of BPA ($mg.L^{-1}$), V is the volume of the solution (L) and m is the mass of the adsorbent (g).

$$Q_E = \frac{(C_0 - C_E)V}{m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Four kinetic models (pseudo-first order, pseudo-second order, Temkin and intraparticle diffusion models) were involved in the determination of the adsorption mechanism of BPA by DAS.

The pseudo-first order kinetic model (Ho and McKay, 2000) is expressed as follows:

$$\ln(Q_E - Q_t) = \ln Q_E - K_1 t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where Q_E and Q_t ($mg.g^{-1}$), are the adsorbed BPA amounts onto DAS at equilibrium and at various times t respectively, and K_1 (min^{-1}) is the rate constant of the pseudo-first order adsorption model. The intercept and slope of the linear plot of $\ln(Q_E - Q_t)$ versus t help to determine the values of Q_E and K_1. The pseudo-second order model (Ho, 2006) is more complete because it takes into account certain decisive steps of adsorption such as external and intraparticle diffusion through the film. This model is well described by equation 3:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_E^2} + \frac{t}{Q_E} \qquad \text{...} (3)$$

where K_2 is the rate constant of the pseudo-second order adsorption model ($g.mg^{-1}.min^{-1}$), Q_E and Q_t are defined as in the pseudo-first order model. The values of Q_E and K_2 are obtained by means of the slope and intercept of the linear plot of t/Q_t versus t.

The Elovich kinetic equation is expressed as in equation 4:

$$Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad \text{...} (4)$$

where α ($mg.g^{-1}.min^{-1}$) and β ($g.min^{-1}$) are the initial adsorption rate and the desorption constant respectively. The slope and intercept of the linear plot of Q_t against lnt yield the values of α and β.

The intraparticle diffusion has often been regarded as the limiting step of most adsorption processes. Equation 5 better reflects this phenomenon:

$$Q_t = K_d t^{1/2} + C \qquad \text{...} (5)$$

where Q_t ($mg.g^{-1}$) and K_d are the instantaneous amount of adsorbate per unit gram of adsorbent and the diffusion constant respectively. C is a constant giving an idea about the thickness of the boundary layer.

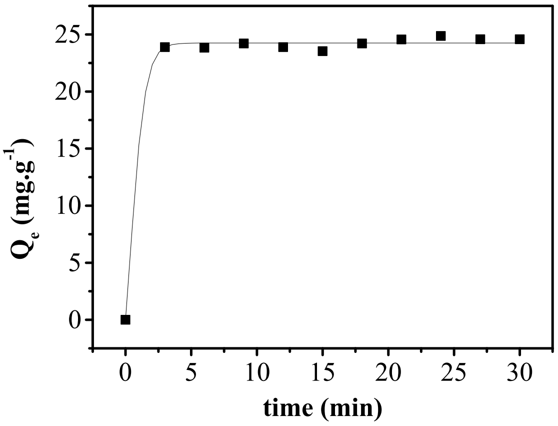


Figure 5. Effect of contact time on the adsorption of BPA by DAS (40 mg of DAS and 15 mL of 60 mg.L^{-1} BPA at 297.2 K, pH 6.0)

Table 4. Kinetic constants and parameters of four adsorption kinetic models for the adsorption of BPA by DAS

Pseudo-first order model	Q_e ($mg.g^{-1}$)	4.4558
	K_1 (min^{-1})	0.2238
	$t_{1/2}$ (min)	3.0972
	R	0.3711
Pseudo-second order model	Q_e ($mg.g^{-1}$)	24.8756
	K_2 ($g.mg^{-1}.min^{-1}$)	0.1206
	$t_{1/2}$ (min)	0.3334
	h ($mg.g^{-1}.min^{-1}$)	74.6267
	R	0.9996
Experimental value	Q_E,exp($mg.g^{-1}$)	24.80
Intraparticle diffusion model	K_{in} ($mg.g^{-1}.min^{-1/2}$)	0.2483
	R	0.7144
Elovich kinetic model	β ($g.mg^{-1}$)	2.6254
	α ($mg.g^{-1}min^{-1}$)	1.1341×10^{26}
	R	0.6547

The values of K_d and C can be determined from the intercept and slope of the linear plot of Q_t versus $t^{1/2}$. The kinetic parameters and correlation coefficients for the removal of BPA by DAS are summarized in Table 4. The correlation coefficient R value for the pseudo-second order model exceeded 0.99, which was much higher compared to that of the other kinetic models which did not exceed 0.7. Furthermore, the experimental adsorption capacity ($Q_{E,exp}$) was also in accordance with the calculated adsorption capacity ($Q_{E,cal}$) obtained from the pseudo-second order model. These results indicated that the pseudo-second order kinetic model fit the adsorption of BPA onto DAS better than did the other models.

BPA adsorption isotherms

The adsorption isotherm indicates how the adsorbed molecules distribute themselves between the liquid phase and the solid phase when the adsorption process reaches equilibrium. Figure 6 shows the adsorption isotherm of BPA on DAS. It can be seen that the adsorption capacity of DAS increased with increasing equilibrium concentration of BPA and reached saturation progressively. This is a well-known adsorption phenomenon where the yield is maximal in a concentrated medium in adsorbate. Moreover, it is not excluded that the more BPA is concentrated, the more its diffusion into the pores of DAS is increased. There are several isothermal models which explain the adsorption phenomena, validated only after experimentation. The model that reflects reality is that with the highest correlation coefficient, but also with the value of the adsorption parameter closest to the experimental value. Models commonly used are that of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. The Langmuir isotherm model ensures a fixation of the adsorbate in a single layer on uniform sites and no subsequent interaction between adsorbed species. Equation 6 gives the linear form of the characteristic equation of this model (Langmuir, 1916):

$$\frac{C_E}{Q_E} = \frac{1}{Q_m K_L} + \frac{C_E}{Q_m} \qquad \text{......................................} (6)$$

where Q_E ($mg.g^{-1}$) is the amount of adsorbate (BPA) adsorbed per unit mass of adsorbent (DAS), C_E ($mg.L^{-1}$) the equilibrium concentration of the adsorbate, Q_m ($mg.g^{-1}$) and K_L ($L.mg^{-1}$) are the monolayer adsorption capacity and the Langmuir adsorption constant respectively. The values of Q_m and K_L are calculated using the intercept and slope of the linear plot of Ce/Q_E versus C_E. The Freundlich isotherm model assumes heterogeneous surface and multilayer adsorption. The related equation is given in the following form (Freundlich, 1906; Alikpokpodion, 2010):

$$\ln Q_E = \ln K_F + \frac{1}{n}\ln C_E \qquad \text{....................................} (7)$$

where K_F and n are the Freundlich constants that represent the adsorption capacity and adsorption strength, respectively; Q_E and Ce are defined as in the Langmuir isotherm. The magnitude of 1/n quantifies the favorability of adsorption and the degree of heterogeneity of the surface. If n > 1, suggesting favorable adsorption, then the adsorption capacity increases and new adsorption sites form (Hameed, 2008). The intercept and slope of the linear plot of lnQ_E versus lnCe help to determine K_F and n.

The linear form of the Temkin isotherm model is (Tempkin and Pyzhev, 1940):

$$Q_E = Q_m \frac{RT}{\Delta Q} \ln K_T + Q_m \frac{RT}{\Delta Q} \ln C_E \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where Q_E is the amount adsorbed at equilibrium, K_T the equilibrium constant and ΔQ the heat of adsorption. By plotting $Q_E = f(\ln C_E)$, one obtains a straight line whose slope and intercept make it possible to determine the heat of adsorption ΔQ and the equilibrium constant K_T.

The Dubinin-Radushkevich isotherm is described by equation 9 (Dubinin and Radushkevich, 1947):

$$Q_E = Q_s e^{-B\varepsilon^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

(9)

The linear form being

$$\ln Q_E = \ln Q_s - B\varepsilon^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

B is a constant relative to the adsorption energy and ε the potential of Polanyi.

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

The value of B is calculated from the slope of the linear plot of $\ln Q_e$ against ε^2. The mean energy of adsorption E ($kJ.mol^{-1}$) is correlated to B by the following relation:

$$E = \frac{1}{\sqrt{2B}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

The energy E determines the dominant sorption process (Maather *et al.,* 2007):

$E < 8$, physisorption dominates the adsorption process.
$8 < E < 16$ ion exchange is the dominant process.
$E > 16$ adsorption is dominated by intraparticle diffusion.

The relative parameters calculated from the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models at 297.4 K are listed in Table 5. On the basis of a comparison of the correlation coefficients R and experimental values of the maximum adsorption capacity Q_m, the Freundlich model fitted the adsorption process better than the other isotherm models. In other words, the adsorption of BPA by DAS took place in a multilayer adsorption manner, the surface of the adsorbent being heterogeneous.

Q_m of DAS for BPA at 297.4 K was 24.5 $mg.g^{-1}$, which was appreciable compared to the values for other non-modified natural adsorbents previously reported in the literature (Table 6). Therefore, DAS seem to be a good BPA adsorbent in aqueous medium.

Effect of the solution pH

The solution pH affects the surface charge of the adsorbent as well as the ionization degree of the adsorbate (Langmuir, 1918; Li *et al.,* 2011).

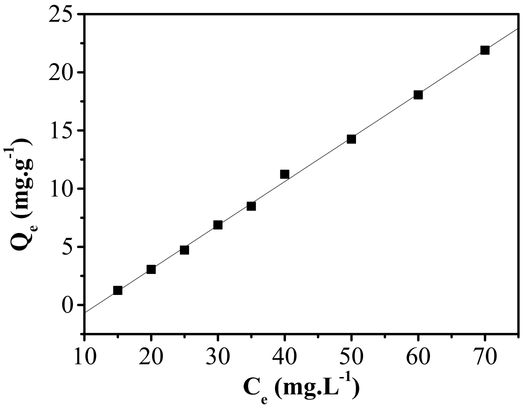


Figure 6. Influence of initial concentration of BPA. Experimental conditions: 15 mL solution, pH 3.0, adsorbent 40 mg; contact time 25 min; stirring speed 200 rpm, room temperature

Table 5. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isothermal constants and parameters

Langmuir (10)	K_L (L.mg^{-1})	0.017
	Q_m (mg.g^{-1})	4.539
	R_L	0.495
	R	0.9346
Freundlich	K_F (mg.g^{-1})	0.0142
	n	0.5649
	R	0.9840
Temkin	b_T	185.281
	B (J.mol^{-1})	13.372
	A_T (L.g^{-1})	0.0615
	R	0.9758
Dubinin-Radushkevich	K_{ad} (mol^2.K^{-1}.J^{-2})	0.0001
	Q_s (mg.g^{-1})	17.8161
	ΔG° (kJ.mol^{-1})	70.71
	R	0.9714

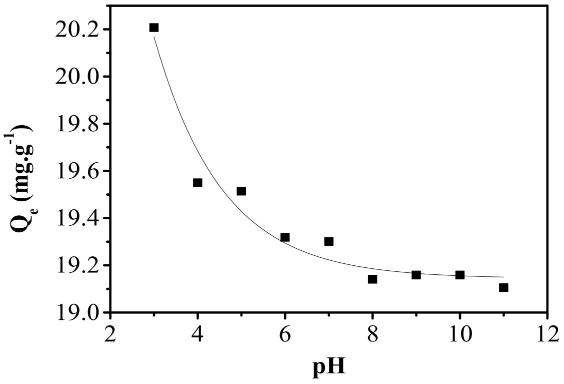


Figure 7. Effect of the solution pH: DAS 40 mg, 15 mL BPA 60 mg/L, contact time 25 min, room temperature

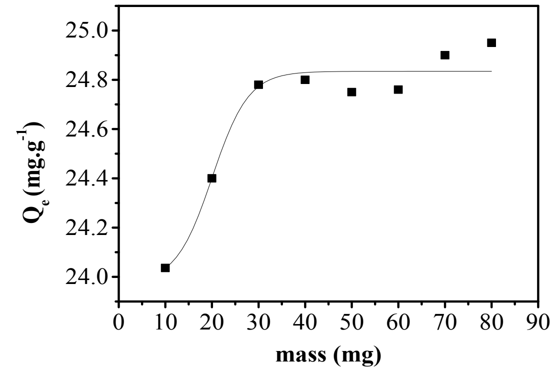
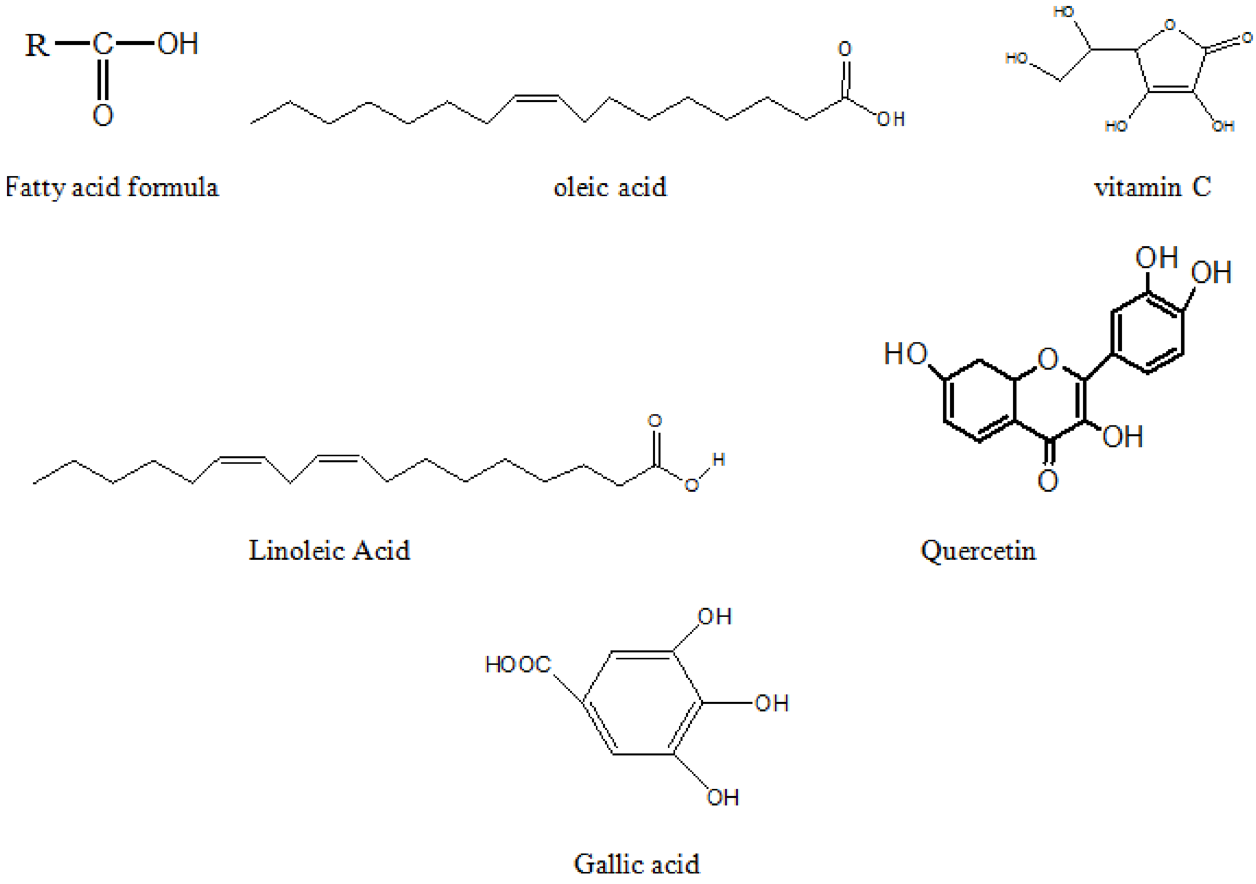


Figure 8. Effect of the adsorbent dosage on the adsorption of BPA by DAS; Experimental conditions: 15 mL of BPA 60 mg.L^{-1}, pH 3, stirring speed 200 rpm, contact time 25 min, room temperature

Table 6. Absorption capacity of DAS compared to other values of the literature

Adsorbent	Temperature (°C)	Adsorption capacity (mg.g^{-1})	Reference
porous carbon obtained at 400 °C from *Phyllostachys pubescens*	23	2.1	Asada *et al.*, 2004
porous carbon obtained at 700 °C from *Phyllostachys pubescens*	23	11.4	Asada *et al.*, 2004
porous carbon obtained at 1000 °C from *Phyllostachys pubescens*	23	41.8	Asada *et al.*, 2004
Graphene oxide	25	87.8	Xu Jing *et al.*, 2013
Activated carbon	23	56.5	Asada *et al.*, 2004
Activated carbon	25	23.5	Nakanishi *et al.*, 2002
Mesoporous silica MCM-41	25	9.0	Kim *et al.*, 2011
Modified carbon nanotubes	7	69.9	Kuo, 2009
Safou seeds powder	25	24.5	This study



Fatty acid formula

oleic acid

vitamin C

Linoleic Acid

Quercetin

Gallic acid

Figure 9. Major components of DAS

Figure 7 shows the effect of the solution pH on BPA adsorption by DAS with the initial pH ranging from 2.0 to 11.0. It should be noted that the DAS adsorption capacity decreases as the pH increases. Indeed, at pH > 5.85 (pH_{pzc}), the surface of the adsorbent is negatively charged. At pH > 8.0 it is BPA which in turn loses its protons and becomes a mono or divalent anion (Bautista *et al.,* 2005). Thus, the relative reduction of the adsorption capacity of DAS observed in the alkaline pH range might be due to the repulsive electrostatic interactions established between the negatively charged surface of DAS and the bisphenolate anion. Maximum adsorption is obtained at pH 3 (20.2 mg.g^{-1}).

At this pH, the DAS surface is surrounded by protons. This gives it a positive overall charge. Since BPA is stable in acidic medium, its adsorption is maximum in acidic medium by formation of hydrogen bond between its hydroxyl groups and those attached to the surface of the material, in addition to the π-π attraction interactions between adsorbate molecules and surface molecules of the adsorbent (Xu and Zhu, 2013).

Effect of adsorbent dosage

The influence of the mass of the biosorbent on the adsorption of BPA was studied by varying the mass from 10 to 80 mg and maintaining the other parameters constant. It appears that the adsorption capacity increases with the mass of the adsorbent (Figure 8) to a value of 24.9 mg.g^{-1} under the experimental conditions. This growth is explained by the increase in the specific surface area of the adsorbent as well as the number of active sites when the mass increases (Nasuha *et al.,* 2010).

Adsorption mechanism: Studies of the African pear (safou) revealed considerable phenolic compounds in the leaves (Ajibesin, 2011) and flavonoids in the pulp (Missang *et al.,* 2003). In a recent study, Ogunmoyole *et al.* (2012) reported the presence of a significant amount of antioxidants (phenols, flavonoids and vitamin C) in safou seeds. In the same way, Otu Okogeri (2016) estimated that the amount of phenolic compounds in safou seeds (33,3 mg GAE/g , Gallic Acid Equivalent) is significantly higher compared to potato peelings

(2,91 mg GAE/g, Mohdaly *et al.,* 2013), *Ocimun basilicum*, *Apium graveolens* and *Lepidium sativum* seeds (51 - 92mg GAE/100 g, Aydemir and Becerik, 2011) and okra (*Abelmoschus esculentus*) seeds (142.48mg GAE/100 mg, Panadda *et al.,* 2010). Ujowundu *et al.* (2010) evaluating the chemical composition of safou (*Dacryodes eudulis*) estimated its carbohydrate content at 37%. Analyzing fatty acids in safou seeds, Ajahi and Adesanwo (2009) estimated that 60% of safou fatty acids are saturated, palmitic acid (C16-0) being the majority (43%); 40% fatty acids are unsaturated, consisting mainly of oleic acid C18-1 (22%) and linoleic acid C18-2 (13%). From the synthesis of these studies, it appears that safou seeds have several surface molecules, which can play a key role in the adsorption process of BPA. In the mechanism that follows, the group of phenolic compounds is represented by gallic acid, the group of flavonoids by quercetin, vitamin C by ascorbic acid, fatty acids by palmitic acid, oleic acid and linoleic acid, the major constituents of safou seeds (Figure 9).

Mechanism involving fatty acid molecules: covalent and hydrogen bond formation

The carboxyl group is the functional group common to saturated and unsaturated fatty acids. In the presence of a molecule carrying an OH group, as is the case with BPA, ester formation occurs (Figure 10). This reaction would effectively contribute to the chemisorption of BPA, covalent bond formation being responsible. Hydrogen bonds would also enhance the adsorbent-adsorbate interactions: CO and OH groups of fatty acids interaction with OH groups of BPA, resulting in the formation of hydrogen bonding (Figure 10).

BPA-fatty acid interactions

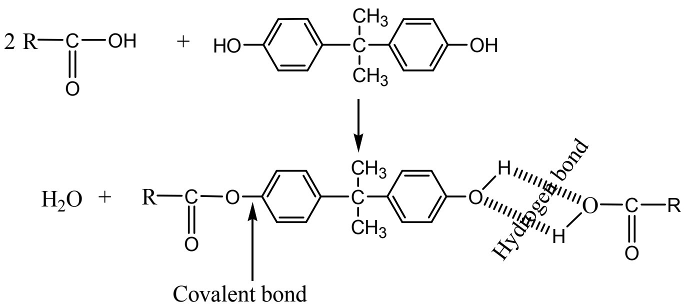
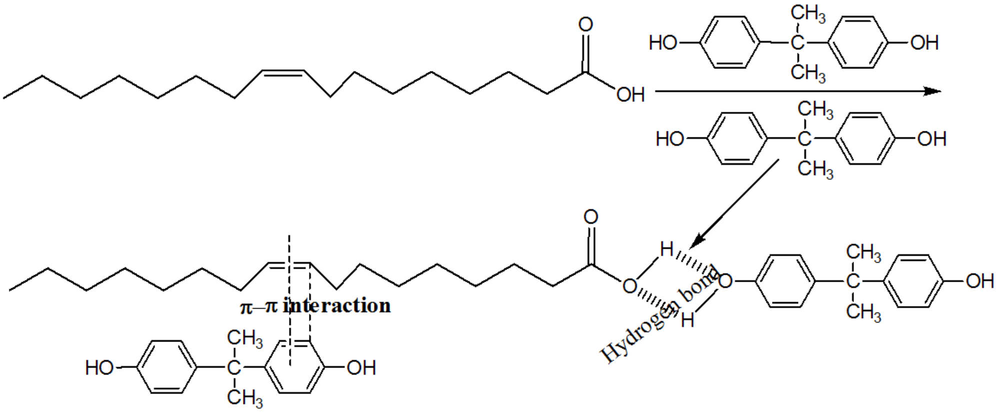


Figure 10. Hydrogen and covalent bonds between BPA and DAS components

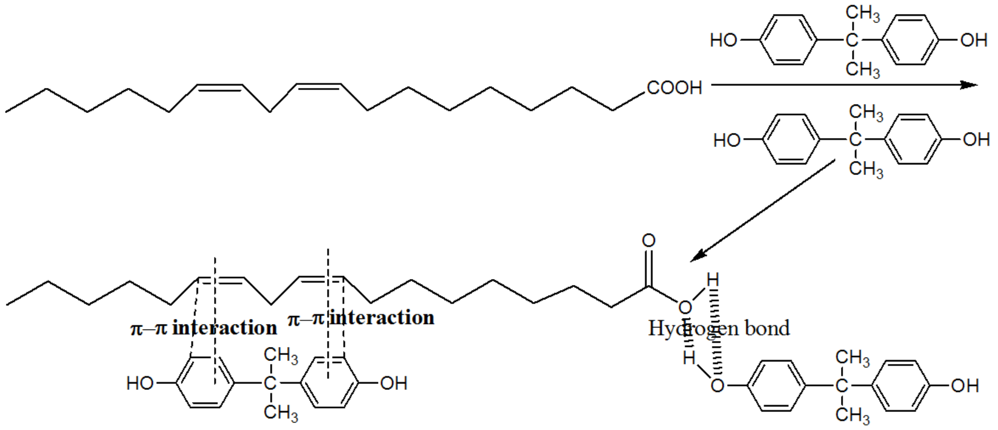
Mechanism involving unsaturated molecules of safou seeds: п-п interactions

Gallic acid, quercetin, ascorbic acid, oleic and linoleic acid are the surface molecules of safou seeds bearing π electrons. On the other hand, BPA is an aromatic compound with 6 π electrons (three delocalized double bonds). The first step of the molecular adsorption mechanism is the transfer of the adsorbate to the external surface of the adsorbent. The adsorbent (safou seeds) with a positive surface charge in acidic medium (pH = 3) attracts the π electrons from BPA to its surface, a rapid step in the adsorption process. The second step is the diffusion of BPA to the internal surface of DAS, a limiting step in the process. The third step is the fixation of BPA in the pores of DAS, a rapid stage of the adsorption process. After adsorption, desorption is possible and can be spontaneous.

BPA-oleic acid interaction



BPA-linoleic acid interaction



BPA-gallic acid interaction

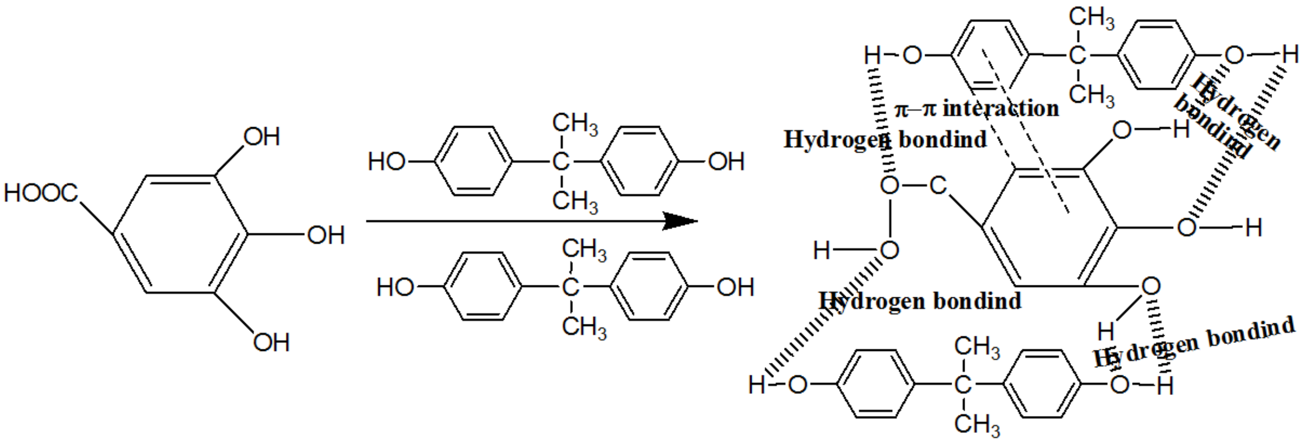
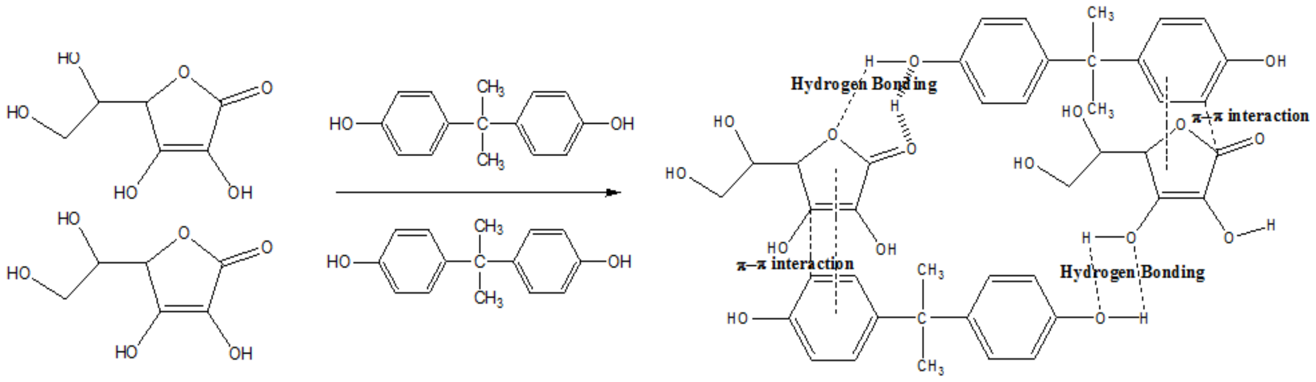
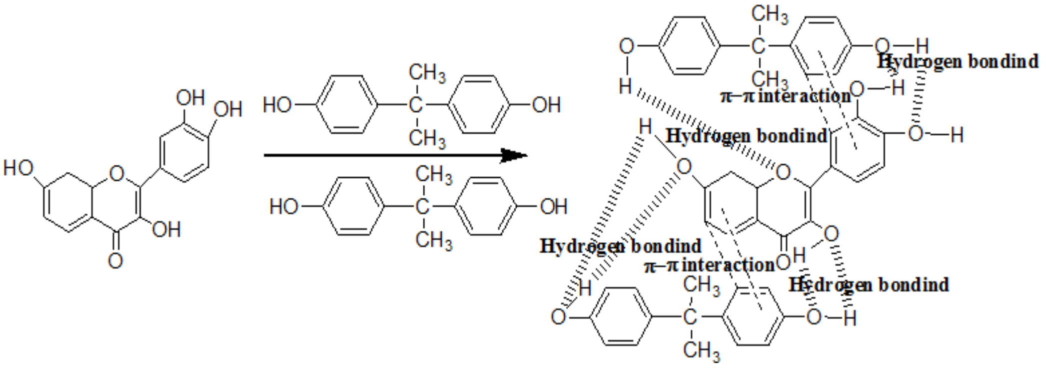


Figure 11. Schematic of hydrogen bonding and π-π interactions between BPA and DAS components

BPA-Vitamin C interaction





It is the adsorption energy that determines the mechanism at this stage. There is physisorption when it is less than or equal to 8 kJ.mol^{-1} and chemisorption when it is greater than or equal to 16 kJ.mol^{-1} (Maather *et al.,* 2007). The adsorption mechanism of BPA by DAS is therefore of the chemisorption type (70.7 kJ.mol^{-1}), supported by adsorbent-adsorbate attracting interactions forces which are the π-π interactions (Figure 11) and those that contribute to the formation of hydrogen bonds and covalent bonding (Figure 10).

Conclusion

Several studies have shown the nutritional and therapeutic nature of safou (*Dacryodes edulis*). In the present study, it is shown that its seeds can be used to remove Bisphenol A from water with satisfactory results. This is a resource, generally considered as waste once the pulp is consumed. What makes this biomaterial suitable for adsorbing Bisphenol A are its varied surface functional molecules. Its low specific surface area would disqualify it if this inconvenience was not compensated by the great heterogeneity of its pores and especially the strong attraction it exerts on Bisphenol A in acidic medium. It is not certain that, by transforming it into activated carbon, its functional groups, determinant in the adsorption process, are conserved. Its adsorption capacity of at least 24.5 mg.g^{-1} and its abundance as waste makes it a potential candidate for the elimination of Bisphenol A and thus the likely elimination of other dreaded phenols such as nonylphenol.

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