

## Optimal removal of bisphenol A by biosorbent based on groundnut (*Arachis hypogaea* L.) shell: Adsorption mechanism, nonlinear kinetics and isotherm.

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### ABSTRACT

Environmental pollution remains as one of the major problems arising from technological development. The discharge of waste water containing this pollutant into the environment without prior treatment has serious consequences for living beings. The objective of this study was to use peanut shells to eliminate BPA in waste water, where, the infrared spectra and diffractograms of materials; and other methods were specifically studied. In this study, the central composite design was used to optimize the factors that affect the adsorption of BPA from solution. These factors include initial concentration, the pH of the solution, the contact time, and the mass of carbon on the response which is the adsorbed quantity of BPA. The respective pH and pHPzc values are 5.99 and 6.34 for the PABs; 6.24 and 7.35 for the PANs and 6.38 and 6.58 for the PAUs. Kinetic studies found the Elovich and pseudo-second-order kinetic models better explain the adsorption mechanism for PABs, PANs, and PAUs. With regards to the adsorption isotherms, the Langmuir, Langmuir-Freundlich and Redlich-peterson isotherms showed a better adsorption capacity for the biosorption of BPA in aqueous solution by PABs, PANs and PAUs with regard to the values of the correlation coefficient and errors.

**Key words:** bisphenol A, biosorption, groundnut shells, isotherm, kinetic.

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### Resumé

La pollution de l'environnement demeure l'un des problèmes majeurs découlant du développement technologique. Le rejet d'eaux usées contenant ce polluant dans l'environnement sans traitement préalable a de graves conséquences pour les êtres vivants. L'objectif de cette étude était d'utiliser des coquilles d'arachides pour éliminer le BPA dans les eaux usées, où, les spectres infrarouges et les diffractogrammes des matériaux ; et autre méthodes ont été spécifiquement étudiées. Dans cette étude, le plan composite central a été utilisé pour optimiser les facteurs qui affectent l'adsorption du BPA de la solution. Ces facteurs comprennent la concentration initiale, la le pH de la solution, le temps de contact, et la masse de carbone sur la réponse qui est l'adsorbé quantité de BPA. Les valeurs respectives de pH et de pHPzc sont de 5,99 et 6,34 pour les PAB; 6.24 et 7.35 pour les PAN et 6,38 et 6,58 pour les PAU. Des études cinétiques ont trouvé l'Elovich et le pseudo-second les modèles cinétiques d'ordre expliquent mieux le mécanisme d'adsorption des PAB, PAN et PAU. Cordialement aux isothermes d'adsorption, les isothermes

de Langmuir, Langmuir-Freundlich et Redlich-peterson ont montré une meilleure capacité d'adsorption pour la biosorption du BPA en solution aqueuse par les PAB, PAN et PAU en ce qui concerne les valeurs du coefficient de corrélation et des erreurs.

**Mots clés :** bisphénol A, biosorption, coques d'arachide, isotherme, cinétique (The abstract was translated by Google Translator and proofread by the Editor)

### Introduction

Pollution generated by anthropogenic activities represents an increasingly worrying threat to humans and ecosystems. Industrial effluents and pollutants resulting from the intensive use of fertilizers, pesticides, sanitary, agricultural and pharmaceutical products are the major causes of environmental pollution. Environmental pollution remains as one of the major problems arising from technological development. Phenolic compounds and their derivatives are recognized as pollutants (Suresh *et al.*, 2011; Liouna *et al.*, 2022).

Pollution concerns all the components (water air and soil) of our environment. Water pollution has taken a prominent place in environmental concerns, given its limited resources and its use in economic development. The use of polymers has undergone significant development over the past decades. Polycarbonates (pc) and epoxy resins are produced in the polymer industry from a monomer called bisphenol A (WHO, 2009). Bisphenol A (BPA) (4,4-(propane-2,2-diyl) diphenol), is an emerging contaminant that is often detected in natural waters at levels of ng/L or µg/L, making it a trace organic contaminant. It is obtained by the reaction between two equivalents of phenol and one equivalent of acetone. Bisphenol A, is found in tap water, surface water, air, and foodstuffs in considerable quantities (Zbair *et al.*, 2017; Ballesteros *et al.*, 2009; Arnold *et al.*, 2013). BPA is a pollutant that mimics the effects of estrogens that are linked to diabetes, cardiovascular disease, breast and prostate cancer, infertility with changes in sperm quality, an endocrine disruptor. and hyperactivity in children (Yun *et al.*, 2018; Wang *et al.*, 2020; Li *et al.*, 2018).

The discharge of waste water containing this pollutant into the environment without any prior treatment is the cause of serious consequences for living beings because they are non-biodegradable. Regarding the fact that specific migration limit for BPA in food is 0.6 µg/g (Cao *et al.*, 2011), it is important to remove BPA from water sources. To overcome this BPA pollution problem, several depollution processes have been set up, which include: ion exchange, membrane filtration, chemical oxidation, adsorption, etc.

Due to the ease of implementation and the performance achieved for various types of pollutants and a wide range of concentrations (Kenne, 2011), adsorption is advantageous compared to other methods. Using adsorption as a depollution method involves biosorption which is a physico-chemical and metabolically-independent mechanisms including absorption, adsorption, ion exchange, surface complexation and precipitation (Marina and Geoffrey, 2014). However, the high cost of the adsorbents used (usually activated carbons) is the main drawback thus, there is a quest to source less expensive adsorbents. Certain agricultural residues (such as peanut shells) most often considered as waste can be used in the adsorption of pollutants such as BPA. The objective of this study was to use peanut shells to eliminate BPA in waste water. For this, we specifically studied:

The infrared spectra and diffractograms of materials; The influence of pH on the materials; The adsorption kinetics (Pseudo-first order and pseudo-second order kinetic model, Elovich model and intra-particle diffusion model); The adsorption isotherms (Langmuir, Freundlich, Redlich-peterson, Sips and Langmuir-Freundlich adsorption isotherm).

## MATERIALS

**Reagents:** Bisphenol A, Urea, Sodium Hydroxide, Chloride Potassium, Oxygenated Water, Ethanol and Distilled Water and peanut shells.

### Equipement

JENWAY brand visible Spectrophotometer; Nicolet iS5 of Thermoscientific branded Infrared Spectrophotometer; A 1/1000b precision balance of brand Sartorius; Bühler GmbH brand Stirring table; Binder brand oven; pH-meter, Filter paper, sieves, conflour grinder, conical flasks, pipets, stopwatch and water bowls.

## METHODS

### Experimental Design

The method of optimization by experimental design is increasingly appealing to researchers because it permits the extraction of maximum information with a minimum of simulation results (Liouna *et al.*, 2022). The central composite design was used in this work to optimize the factors that affect the adsorption of BPA from solution. These factors include initial concentration, the pH of the solution, the contact time, and the mass of carbon on the response which is the adsorbed quantity of BPA. These experimental quantities can be simulated by kinetic or isotherm models. To properly describe and model the kinetic and isotherm adsorption, two methods exist: the nonlinear method and the linear method. Recent works have shown that nonlinear regression produces very satisfactory results compared to linear regression (Shikuku *et al.*, 2018 and Bopda *et al.*, 2019). Thus, for the nonlinear regression, the selection of the error functions showed a remarkable change in terms of the values of the constants linked to the models studied, as demonstrated by Kamgaing *et al.*, 2017 and Ngakou *et al.*, 2019.

### Preparation of adsorbent

Peanut shells used were collected from farmers in the town of Bandjoun (Western Cameroon

region). Groundnut (*Arachis hypogaea*), is a Fabaceae (*legumes or papilionaceae*) cultivated for its seeds. When shelled, the seeds are used for nutrition in different forms and peanut shells are waste products of the shelling process.

The peanut shells were cleaned several times under running tap water, then dried in the sun for 24 hours. They were then ground using a corn flour machine. The powder obtained was sieved using a 100 $\mu$  sieve giving powder with uniform particle size of less than 100 microns. The powder washed was washed in clean water, then rinsed with distilled water. The resulting pulp was dried in an oven at 100° C for 24 hours to remove all water.

### Chemical treatment of the material with urea

A mass of 10 g of the powdered biosorbent obtained was introduced into a 100 mL glass bottle inside which a 30 mL and 0.06 M urea solution was introduced beforehand. The bottle was then brought under stirring using a stirring table at a stirring speed of 200 rpm for one hour and then was filtered. The biosorbent obtained was washed abundantly with distilled water and then placed in an oven at 100° C. for 24 hours to eliminate traces of water. This is what was used as the adsorbent.

### Chemical treatment of the material with soda

10g of the powdered biosorbent were poured into a 100mL conical flask containing 30mL of 0.06M sodium hydroxide (NaOH) solution. The flask was then stirred using a stirring table at a speed of 200 rpm for one hour and then the resulting solution filtered using a filter paper. The biosorbent obtained was washed abundantly with distilled water to remove all the NaOH solution and then dried in an oven at 100° C for 24 hours.

### Characterization of materials by infrared spectroscopy

The materials (untreated and treated) were characterized by infrared spectrophotometry to identify the functional groups present on their

surfaces. The infrared domain was characterized by radiation whose wavelength was between 0.8 and 1000  $\mu\text{m}$ .

IR is an analytical technique that uses small quantities of sample, it is non-destructive and fast. IR spectrophotometry includes the ATR (Attenuated Total Reflection) method, which is a reflection technique in which an internal reflection optical device with a high refractive index is used for the measurements.

For the analysis, five milligrams of the treated and untreated materials were deposited on the measuring surface consisting of a germanium crystal. After pressing the sample in the IR device, the recording of the infrared spectrum was noted.

### **Characterization of materials by X-ray diffraction**

X-ray diffraction (XRD) is a technique used in determining the structure of complex natural substances. It is a convenient, practical and exceptional method to provide qualitative and quantitative information concerning the compounds present in a solid sample. The technique makes it possible to determine the interatomic distances and the arrangement of atoms in crystal lattices. As the X-rays are diffracted in a different way by the elements of the network according to the construction of the latter, the irradiation of the material by X-rays makes it possible to know its crystallographic nature. The scattering power of X-radiation by an atom depends on its electron density, located around its nucleus.

For analysis, five milligrams of the materials were placed in a transmission geometry using a STOE Stadi-p brand powder diffractometer (STOE and Cie GmbH, Darmstadt Germany) with a copper anticathode delivering a Cu  $K\alpha_1$  filtered radiation with a wavelength of 1.54056  $\text{\AA}$ , under an acceleration voltage of 40 KV and an intensity of 30 mA. The recording range was between 5°

and 55° in (2 $\theta$ ) mode with a step of 0.033°. The measurements were performed for a calculation time of 200 seconds per step with a scan speed of 5°/min.

### **Determination of the pH at the point of zero load of the biosorbent**

The pH at the point of zero charge (pH<sub>pzc</sub>) corresponds to the pH value for which the overall charge on the surface of a material is zero. It is a significant factor that indicates the adsorption ability of a material and the type of active sites on its surface. The pH<sub>pzc</sub> makes it possible to determine the acidic or basic character of the adsorbent, and to know, according to the pH of the solution, the net charge of the latter. When pH of the solution > pH<sub>pzc</sub>, adsorption is favorable for cationic pollutants and when pH of the solution < pH<sub>pzc</sub>, adsorption is favorable for anionic pollutants and material surface is positively charged (Ta and Chi, 2016).

In order to determine the pH<sub>pzc</sub>, 30 mL of Potassium chloride solution of 0.1M concentration was introduced into five different flasks and their initial pH values were respectively adjusted to 2, 4, 6, 9 and 10. Then, 25 mg of the bioadsorbent material were introduced into each of the flasks and the whole was stirred for 24 hours. After decantation, the final pH of each flask was measured. The plotting of the curve pH<sub>initial</sub> - pH<sub>final</sub> = f (pH<sub>initial</sub>) made it possible to determine the pH<sub>pzc</sub> which is the intersection between the curve obtained and the abscissa axis.

### **Bisphenol biosorption in batch mode**

BPA is sparingly soluble in water, soluble in ethanol and stable in hydrogen peroxide medium. Due to this, a solution of BPA (250 mL, 500 mg/L) was obtained by dissolving a known mass of this compound in a solution of ethanol and hydrogen peroxide (30% v/v and 10%v/v respectively). Daughter solutions ranging from 50 to 100 mg/L

were prepared from the stock solution. The initial pH was adjusted using 0.2 mol/L acid and base solutions. All adsorption experiments were carried out at a temperature range of 25°C to 55°C.

**Kinetic**

The study of adsorption kinetics provides information on the different stages of the adsorption process between the particles of the adsorbate and those of the adsorbent as a function of time. The pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich kinetic model were applied to the experimental data obtained after studying the influence of contact time on the biosorption of BPA.

**Data Analysis**

The data was analysed using the nonlinear regression method and adding some error functions, the validity of the mathematical adsorption models with the experimental results was evaluated.

**RESULTS AND DISCUSSION**

**RESULTS**

**Infrared spectrum of materials**

As presented on figures 1, 2 and 3, the spectra have the same shape. This is proof that all materials have essentially identical functional groups.

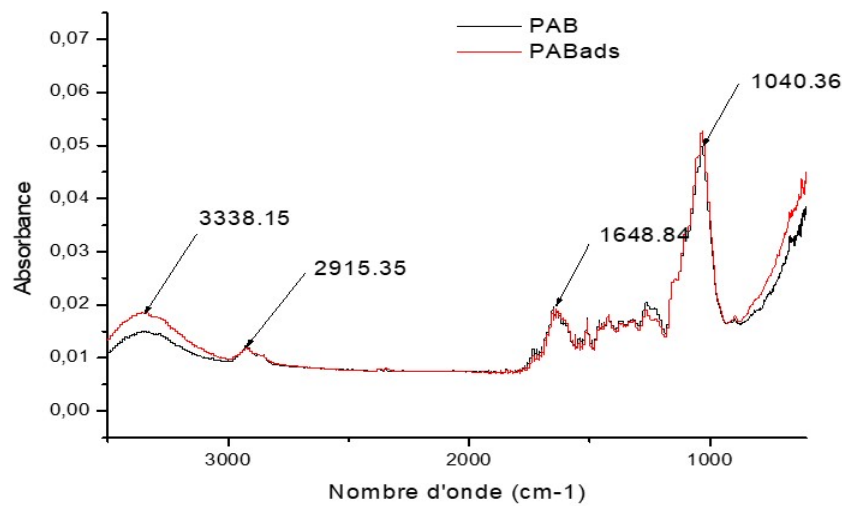


Figure 1: IR spectrum of raw peanut shells before adsorption (PAB) and after adsorption (PABads).

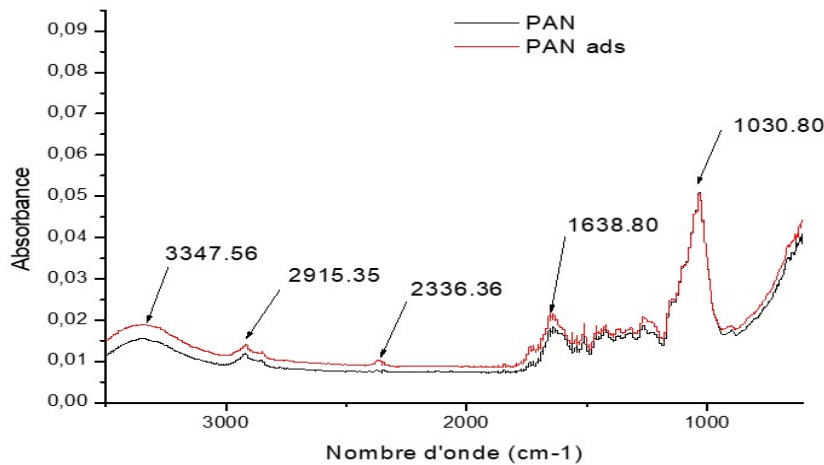
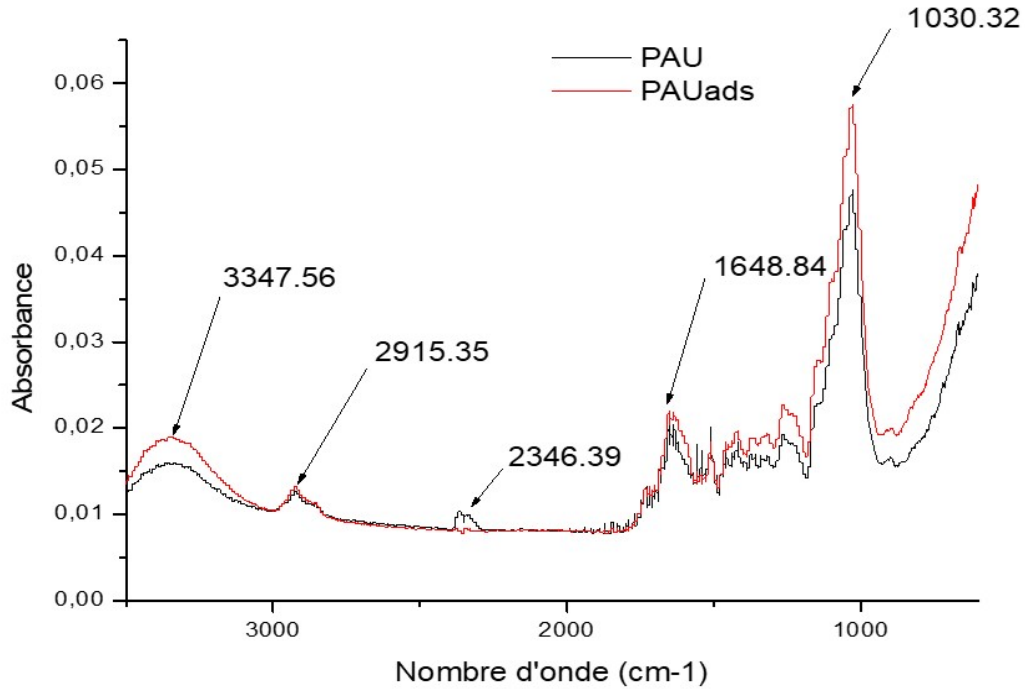


Figure 2: IR spectrum of peanut shells treated with sodium hydroxide before adsorption (PAN) and after adsorption (PAN ads).



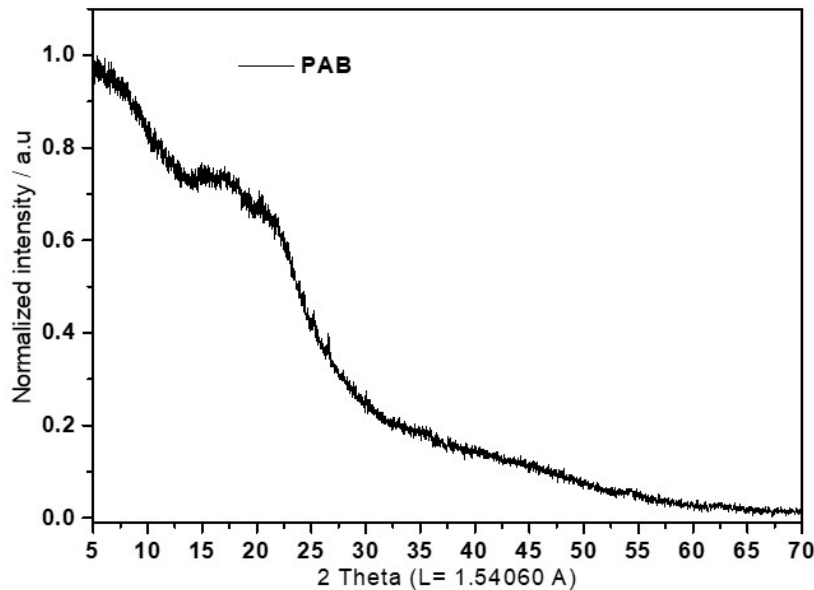
**Figure 2:** IR spectrum of peanut shells treated with sodium hydroxide before adsorption (PAN and after adsorption (PAN ads).

**Characterization by X-ray diffraction**

Figures 4, 5 and 6, show the characterization of PAB, PAU and PAN by the x-ray diffraction method. From the figures there are no peaks for PAB, PAN or PAU. This observation confirms the amorphous nature of lignocellulosic material, which is an advantageous property for adsorption processes and indicative of a porous structure (Homchan *et al.*, 2011).

**pH and pH at point of zero charge (pHpzc) of materials**

The pH<sub>pzc</sub> values obtained as shown on figure 7 are 6.34, 6.58 and 7.35 respectively for the PAB, the PAU and the PAN. In solutions with pH values lower than these, the materials (PAB, PAN and PAU) will be positively charged and otherwise they will be negatively charged.



**Figure 4:** PAB powder diagram

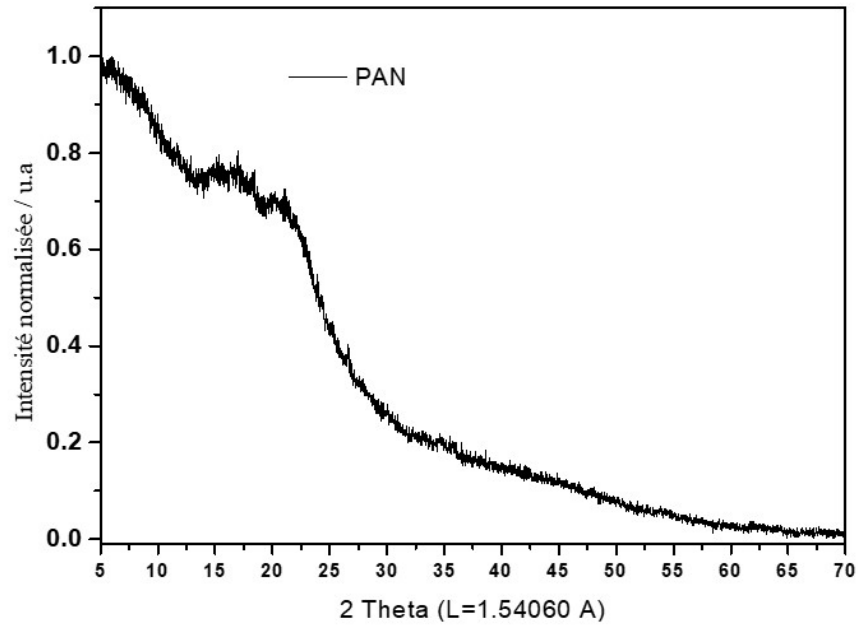


Figure 6: PAU powder diagram

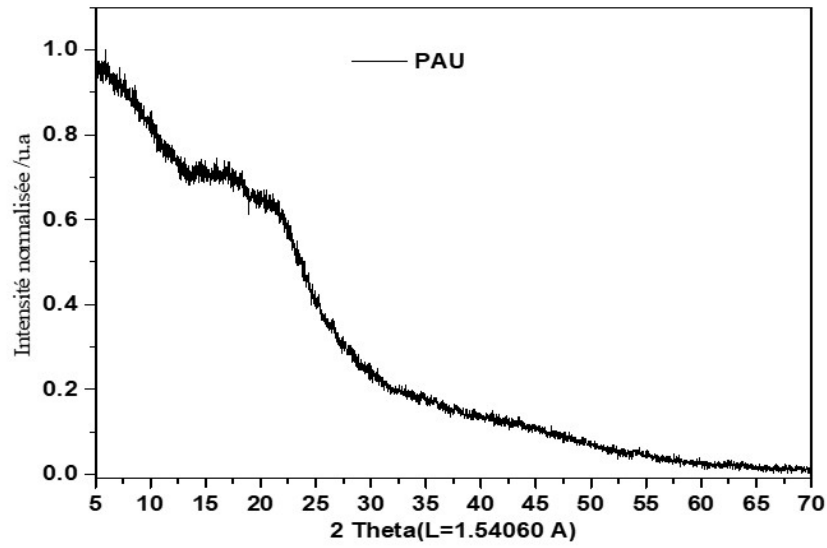


Figure 6: PAU powder diagram

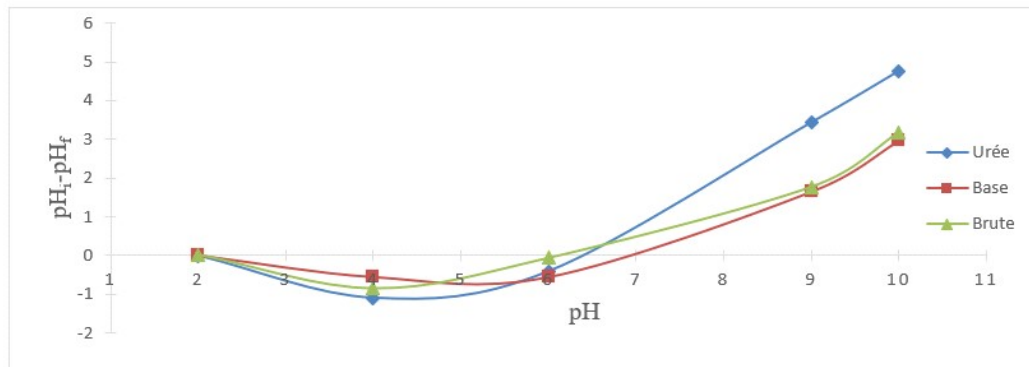


Figure 7: Variation of initial pH and final pH as a function of initial pH (30 mL of 0.1M solution, 25 mg of adsorbent, V=200 rpm for 24 hours)

**Kinetic studies****Table 1:** Summary of the different constants of the kinetic models studied

	Models	Constants	values	R <sup>2</sup>	RRMEQ	$\chi^2$	FEFH	ERM	SEA
<b>PAB</b>									
1.	Pseudo first order	Qe (mg/g)	15.718	0.948	3.441	0.859	10.684	6.79	9.637
		K1 (1/min)	0.210						
2.	Pseudo second order	Qe (mg/g)	16.897	0.986	1.782	0.239	2.949	3.403	4.757
		K2 (g/min.mg)	0.021						
3.	Elovich	$\alpha$ (mg/g.min)	195.171	0.988	0.758	0.038	0.481	1.522	2.391
		$\beta$ (g/mg)	0.538						
4.	Diffusion	Kid (mg/g.min <sup>0.5</sup> )	1.332	0.553	8.455	8.788	27.158	10.798	21.782
		C(mg/g)	6.382						
<b>PAN</b>									
1.	Pseudo first order	Qe (mg/g)	18.797	0.936	4.623	1.367	16.433	7.996	13.373
		K1 (1/min)	0.173						
2.	Pseudo second order	Qe (mg/g)	20.448	0.980	2.588	0.426	5.218	4.291	7.138
		K2 (g/min.mg)	0.013						
3.	Elovich	$\alpha$ (mg/g.min)	73.637	0.985	1.094	0.071	0.890	1.741	2.972
		$\beta$ (g/mg)	0.383						
4.	Diffusion	Kid (mg/g.min <sup>0.5</sup> )	1.673	0.667	9.181	9.379	27.689	10.012	23.540
		C(mg/g)	6.911						
<b>PAU</b>									
1.	Pseudo first order	Qe (mg/g)	17.463	0.925	4.708	1.745	19.625	8.508	12,637
		K1 (1/min)	0.159						
2.	Pseudo second order	Qe (mg/g)	19.019	0.972	2.841	0.618	7.318	5.110	7.473
		K2 (g/min.mg)	0.013						
3.	Elovich	$\alpha$ (mg/g.min)	50.809	0.963	1.659	0.189	2.367	2.960	4.431
		$\beta$ (g/mg)	0.396						
4.	Diffusion	Kid (mg/g.min <sup>0.5</sup> )	1.567	0.685	8.357	8.445	25.682	9.938	21.408
		C(mg/g)	6.191						

Kinetic models such as the pseudo-first order, pseudo-second order, Elovich, and intraparticle diffusion models were investigated. The nonlinear plots are shown in Figures 8, 9 and 10. Table 1 shows the calculated values

of all parameters. It emerges that the nonlinear kinetic pseudo-first order, pseudo-second order, and Elovich models are more appropriate for the description of the adsorption of bisphenol A on the PAB, PAN and PAU, because the coefficients of determination are closer to unity. However, the low value of  $\div 2$  and the low values of the error functions obtained from the Elovich model show that it is the best kinetic model to describe the adsorption

of BPA. This model suggests that the adsorption of BPA is primarily chemical and the active sites on the surface of PAB, PAN and PAU are heterogeneous (Bopda *et al.*, 2019). This is confirmed by the values of the desorption constant  $\hat{a} \hat{A} 1$ . Observation of the pseudo-first order kinetic model (Figures 8, 9 and 10) shows that the binding of BPA molecules to the surface of PAB, PAN and PAU occurs rapidly, there by reaching equilibrium. For pseudo-second order kinetics, the amounts adsorbed at equilibrium are close to experimental ones, which demonstrates the existence of majority  $\delta$ - $\delta$  type interactions (Tran *et al.*, 2017)



**Influence of concentration**

*Table 2: Summary of the different constants of the isotherms used*

No.	Models	constants	values	R <sup>2</sup>	RRMEQ	χ <sup>2</sup>	FEFH	ERM	SEA
<b>PAB</b>									
1.	Langmuir	Qm (mg/g)	140,820	0.990	0.498	0.04	0.932	1,607	0.710
		KL	0.00020						
2.	Freundlich	KF	0.030	0.92	1,860	0.522	11,218	7,900	3,857
		Not	0.758						
3.	Redlich-Peterson	A (L/g)	0.787	0.916	1,924	0.561	15,999	8,184	3,995
		B (L/mg)	30,039						
		B	-0.391						
4.	Sips	Ks (L/g)	40,485	0.989	0.491	0.033	1,082	2,212	1,054
		as (L/g)	0.00165						
		Bs	1,202						
5.	Langmuir-Freundlich	qMLF	52,333	0.990	0.466	0.028	0.939	2,051	0.984
		KLF	0.00335						
		MLF	1,109						
<b>PAN</b>									
1.	Langmuir	Qm (mg/g)	96,899	0.990	0.687	0.039	0.980	2018	1,453
		KL	0.00043						
2.	Freundlich	KF	0.302	0.992	0.583	0.028	0.727	1,778	1,263
		Not	1,137						
3.	Redlich-Peterson	A (L/g)	1,510	0.993	0.543	0.0241	0.812	1,584	1,119
		B (L/mg)	4,763						
		B	0.102						
4.	Sips	Ks (L/g)	58,318	0.992	0.567	0.0244	0.833	1,431	1.075
		as (L/g)	0.0019						
		Bs	1,163						
5.	Langmuir-Freundlich	qMLF	72,360	0.993	0.557	0.0240	0.813	1,494	1,109
		KLF	0.00035						
		ML	1,102						
<b>PAU</b>									
1.	Langmuir	Qm (mg/g)	22,120	0.984	0.766	0.040	1.045	6.973	4,744
		KL	0.0019						
2.	Freundlich	KF	0.308	0.827	2,463	0.537	12,195	6,283	4,261
		Not	1,096						
3.	redlich peterson	A (L/g)	1,486	0.827	2,461	0.536	16,239	6,289	4,264
		B (L/mg)	3,993						
		B	0.183						
4.	Sips	qms (L/g)	4,467	-4.303	5,377	2,604	78,843	14,514	9,424
		Ks (L/g)	1,438						
		Ms	0.273						
5.	Langmuir-Freundlich	qMLF (mg/g)	13,456	-5.684	5.957	3,243	97,336	16,280	10,638
		KLF	1,184						
		MLF	0.326						

PAU									
1.	Langmuir	Qm (mg/g)	22,120	0.984	0.766	0.040	1.045	6.973	4,744
		KL	0.0019						
2.	Freundlich	KF	0.308	0.827	2,463	0.537	12,195	6,283	4,261
		Not	1,096						
3.	redlich peterson	A (L/g)	1,486	0.827	2,461	0.536	16,239	6,289	4,264
		B (L/mg)	3,993						
		B	0.183						
4.	Sips	qms (L/g)	4,467	-4.303	5,377	2,604	78,843	14,514	9,424
		Ks (L/g)	1,438						
		Ms	0.273						
5.	Langmuir-Freundlich	qMLF (mg/g)	13,456	-5.684	5.957	3,243	97,336	16,280	10,638
		KLF	1,184						
		MLF	0.326						

As presented on table 2, the following were deduced:

#### Case of PAB

The correlation coefficient value of 0.990, the low values of  $\div 2$  and calculated error functions show that the Langmuir and Langmuir-Freundlich isotherms best explain the biosorption of Bisphenol A. The Langmuir-Freundlich isotherm includes knowledge of adsorption on heterogeneous surfaces. Since the Langmuir isotherm has a correlation coefficient close to unity, we can say that the Langmuir-Freundlich isotherm reduces to Langmuir's equation (Zbair *et al.*, 2017). The latter suggests a distribution of the molecules of the adsorbent in the form of a monolayer on a homogeneous surface; however, the kinetics of this material with the Elovich kinetic model suggests the opposite (the sites of the biosorbent are heterogeneous).

#### Case of PAN

The correlation coefficient value of 0.993, the low values of  $\div 2$  and calculated error functions, show that the Redlich-peterson and Langmuir-Freundlich isotherms better explain the adsorption of BPA.

#### Case of PAU

The correlation coefficient value of 0.984, the low values of  $\div 2$  and calculated error functions,

show that the Langmuir isotherm predominates. The Langmuir isotherm suggests a distribution of adsorbent molecules in the form of a monolayer on a homogeneous surface; however, the kinetics of this material with the Elovich kinetic model suggests the opposite (the sites of the biosorbent are heterogeneous).

## DISCUSSIONS

### Infrared spectrum of materials

During the biosorption reaction, the –OH group of the pollutant (BPA) binds to the surface of the material, hence the increase in intensity of the peak at 3338-3347 cm<sup>-1</sup> after adsorption on the various figures attesting materials bind BPA. The treatment of the raw material with soda (see figure 2) is at the origin of the appearance of a slight peak at 2336.36 cm<sup>-1</sup> which is characteristic of the –C=O groups of the carboxylates which intensifies after adsorption. On the other hand, during the treatment with urea, the group (CO(NH<sub>2</sub>)) of the urea attaches to the surface of the material, hence the appearance of the peak at 2346.39 cm<sup>-1</sup>. After adsorption, this peak disappears due to its hydrolysis. This result is equally reported by (Kamgaing *et al.*, 2017)

### Characterization by X-ray diffraction

The results suggest that the amorphous character is a privileged property to better define adsorbents from biomass (Kamgaing *et al.*, 2017). The

absence of peaks shows that the different materials are amorphous.

**pH and pH at point of zero charge (pH<sub>pzc</sub>) of materials**

When the pH of the solution is lower than the pH<sub>pzc</sub> of the material, adsorption is favorable for an anionic analyte. Otherwise, it is favorable for a cationic analyte (Ta and Chi, 2016). This indicates why the surface charge of the material

is positive because pH of the solution was = 5.56 (6.34, 6.58 and 7.35 > 5.56).

**Kinetic studies**

From the results of the kinetic studies presented on table 1 and figures 8,9 and 10, the Elovich model, and the pseudo-second-order kinetic model are better since the value of the calculated adsorbed quantity is close to that obtained experimentally.

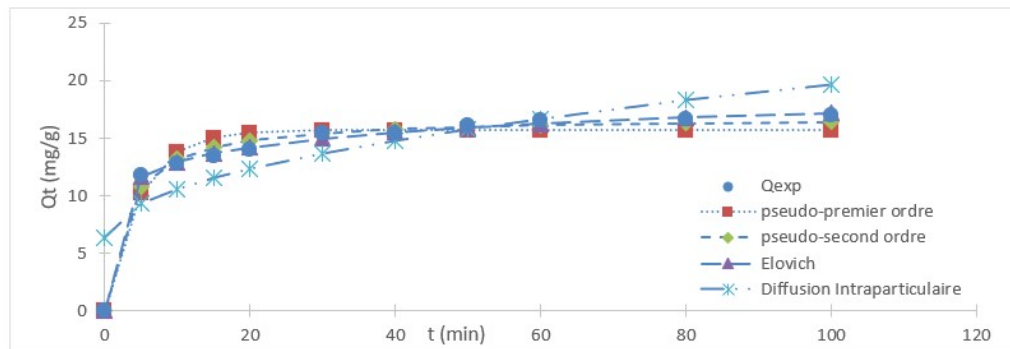


Figure 8: Non-linear regression method of PAB adsorption kinetics

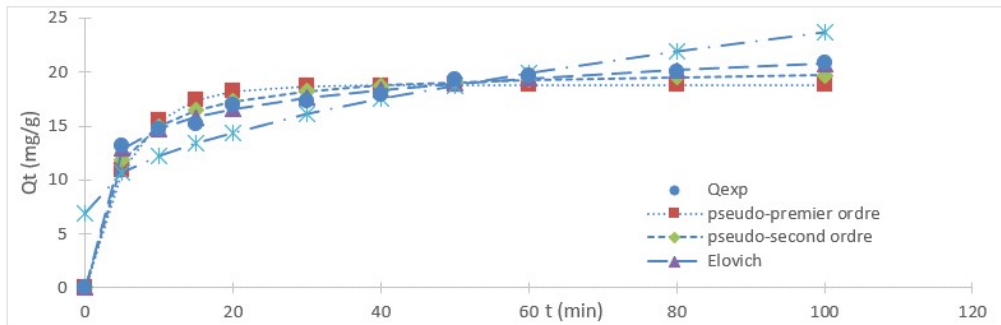


Figure 9: Non-linear regression method of PAN adsorption kinetics

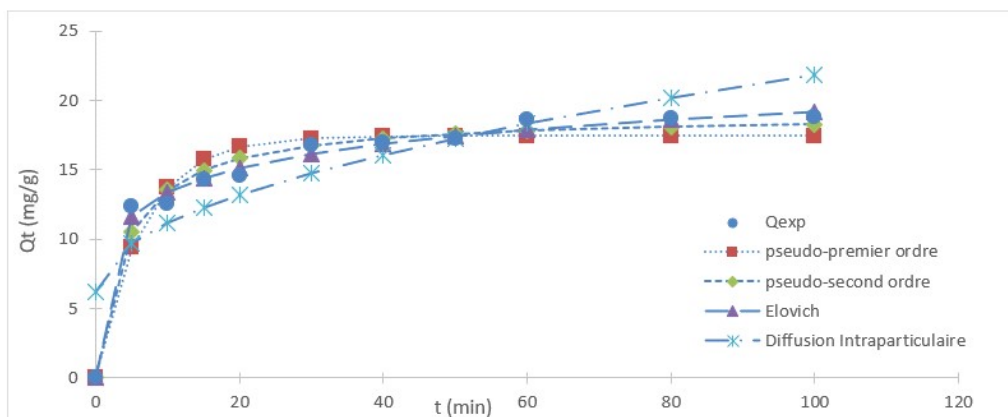


Figure 10: Non-linear regression method of PAU adsorption kinetics

## Influence of concentration

### Case of PAB

The PAB case could be explained by the coexistence of adsorption and desorption phenomena during the biosorption of BPA by PAB.

### Case of PAN

For a value of  $\hat{\alpha} = 0.102 \cdot 1$  the Redlich-Peterson isotherm does not reduce to the Langmuir equation but to that of Freundlich, which is only applicable for processes of adsorption that take place on heterogeneous surfaces. Since the Langmuir-Freundlich isotherm includes knowledge of adsorption on heterogeneous surfaces, we can say that the surface of PAN is heterogeneous.

### Case of PAU

The Langmuir isotherm suggests a distribution of adsorbent molecules in the form of a monolayer on a homogeneous surface; however, the kinetics of this material with the Elovich kinetic model suggests the opposite (the sites of the biosorbent are heterogeneous). This could be explained by the coexistence of adsorption and desorption phenomena during the biosorption of BPA by PAU. The value of  $n=1.196$  obtained from the Freundlich isotherm reflects a high affinity between the molecules of BPA and PAU. The negative values of the  $R^2$  correlation coefficients obtained by the Sips and Langmuir-Freundlich model show that the process of adsorption of BPA in aqueous solution with PAU is not possible.

## CONCLUSION

The experiments carried out focused on the optimization of the biosorption of biophenol A in aqueous solution by peanut shells. The choice of this residue was based on its lignocellulosic nature and its availability after harvest.

Part of this material was treated with soda, another with urea and the various characterizations made allowed us to know the chemical functions that PABs, PANs and PAUs have on their surface. The respective pH and pHPzc values are 5.99 and 6.34 for the PABs; 6.24 and 7.35 for the PANs and 6.38 and 6.58 for the PAUs.

The optimal conditions were met for 500 mg of adsorbent whose particle diameter is less than 100  $\mu\text{m}$ , a pH of the adsorbate solution equal to 2, an adsorbate concentration in solution equal to 100 mg/L and an equilibrium time of 60 minutes at a stirring speed of 200 rpm. Some kinetic and adsorption isotherm models were applied to the data obtained experimentally.

Kinetic studies found the Elovich and pseudo-second-order kinetic models better explain the adsorption mechanism for PABs, PANs, and PAUs. With regards to the adsorption isotherms, the Langmuir, Langmuir-Freundlich and Redlich-peterson isotherms showed a better adsorption capacity for the biosorption of BPA in aqueous solution by PABs, PANs and PAUs with regard to the values of the correlation coefficient and errors.

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### Conflict of Interest

We declare that there is no conflict of interest among all authors of this work.

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