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Removal of Carbamazépine (CBZ) from aqueous solution using Cuttlefish bones

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Abstract

Pharmaceutical compounds have an emerging group of organic pollutants in aquatic systems. Among many used PCs, the most frequently detected compounds is carbamazepine (CBZ).This work investigate the possibility of elimination of carbamazepine (CBZ) from aqueous solutions using cuttlefish bone powder (CFPB) as an adsorbent material by studying the effect of various equilibrium parameters like contact time, pH effect, concentration variation and temperature using a simple technique which is UV. The results obtained showed that sorption on the cuttlefish bone could be a powerfull method for the removal of Carbamazépine (CBZ). The efficacy of cuttlefish bone in the elimination of Carbamazépine (CBZ) from aqueous solutions is about 95 % at pH 9. The kinetic results of adsorption are described better by using the model of pseudo second order. Unlike The isotherm of adsorption of Carbamazépine (CBZ) is described very well by the model of Freundlich. The thermodynamic parameters obtained indicate that the adsorption of CBZ on the cuttlefish bone powder (CFPB) is a spontaneous and endothermic process. Surface morphology and crystalline nature of the prepared sorbent were characterized by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), scanning electron microscopy (SEM) and Fourier Transform Infrared (FTIR) spectroscopy.

Keywords: adsorption, Carbamazépine, cuttlefish bone, Characterization, equilibrium, kinetics, thermodynamics

Contents

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1. Introduction

In recent years, the presence and the future of drug residues and their metabolites in different compartments of the aquatic environment: wastewater, groundwater, surface water and drinking water [1-5], have become a topic of public interest. A wide variety of PPCPs and their metabolites are continuously introduced into the environment by human waste excretion, washing, manufacturing, etc. They are widely detected in aquatic ecosystems [6-9], at

different levels which can vary from ng L^{-1} to µg L^{-1}, but continuous release and fugitive emissions of these residues are persistent micro-contaminants [10]. Among the many PCs in use, one of the compounds is the most frequently detected; it's the carbamazepine (CBZ). This drug is an anticonvulsant first generation that has been used worldwide to treat partial seizures, trigeminal neuralgia, the manic-depressive illness and explosive aggression for nearly 40 years [11].

The removal efficiency of CBZ by degradation and / or retention processes in conventional WWTPs has been found to be very low and can be attributed to its resistance to biodegradation [12-15], In effect, the CBZ was measured repeatedly in wastewater in irrigated agricultural soils with TWW [16], in surface waters (Ternes, 1998; Andreozzi et al., 2003; Metcalfe et al., 2003; Wiegel et al., 2004) and groundwater [17]. The level of CBZ concentration detected in the environment range from 30 ng L^{-1} in drinking water to 6.3 g L^{-1} in wastewater [14]. There are several methods for the removal of carbamazepine, such as UV treatment followed by biological treatment [18], activated carbon filtration, ozonation and flocculation [19].

Among many methods available the adsorption process is one of the most promising techniques for the removal of contaminants [20]. The advantages of adsorption process, compared to other separation processes, are its simplicity and flexibility in design and operation. This process is inexpensive and can produce a free contaminant effluent for reuse [21]. Although the activated carbon is one of the most widely studied adsorbents for the control of environmental pollution, the main disadvantage of activated carbon is its high production and treatment costs. In addition to cost, adsorption characteristics and availability are also from basic parameters in adsorbent selection. Thus, many researchers throughout the world have focused their efforts on optimizing the adsorption and developing novel alternative adsorbents with high absorptive capacity and low cost [20, 22].

Studies have shown that absorbents include clay materials [23], chitosan [24], which could effectively remove the dyes from wastewaters in this study, an adsorbent newly identified, inexpensive and readily available, which the cuttlefish is. It is a marine animal closely related to octopuses, squids, and nautilus species collected from the Sea of Bizerte. The scientific name of the cuttlefish Sepia latimanus. Cuttlefish are generally within a size range from 15 to 25 cm, containing within bone 10 to 20 cm in size. Cuttlefish bone, also known as cuttlefish bone, is a hard, brittle material and structured internally.

2. Materials and Methods

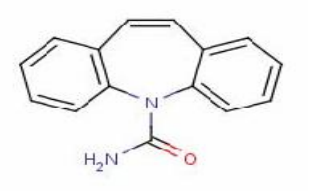
The target adsorbent was prepared in the laboratory. Cuttlefish bone was rinsed with demonized water, boiled for 10 min. To desorb any impurities, it was dried at 103–105 ˚C for 24 h and allowed to cool in a desiccator [25]. In our study, cuttlefish bone was crushed and pulverized, by standard ASTM sieves (range being 60 to 100 meshes), into 150-250 µm particles and used as an adsorbent in the following experiments [26]. The drugs carbamazépine (CAS: 298-46-4) solutions with different concentrations were prepared by diluting the stock solution in distilled water. The maximum absorption wavelength of the drugs (λmax) was determined by absorbance spectrum detection between 200 nm to 800 nm using the UV/Vis spectrophotometer (model of SP-3000 Plus). The curve of absorption plaines, λmax of Carbamazépine (CBZ) is 271 nm.

The X-ray diffraction pattern of the cuttlefish bone was recorded by X'Pert PRO MPD working on monochromatic radiation Copper Kα1 (1.5406 Å). A counter (PM 8203) records a signal proportional to the intensity of the diffracted beam. Elemental analysis was conducted by à Magix PW2403 wavelength dispersive sequential XRF (X-ray fluorescence) analyzer. The Brunauer–Emett–Teller (BET) surface area was determined by the low temperature N_2 adsorption method. The degradation temperature was determined by thermogravimetric analysis using a Thermal Analyzer Mettler Toledo. The sample of ca. 25.3 mg was placed in a alumina pan and heated up to 610 °C under air at a heating rate of 5 °C/min.

To gain further insight into the microstructures, TEM investigations were performed using a Tecnai ultra Twin G2-Philips. Samples for analysis were prepared by air-drying a drop of a sonicated suspension of the dried precipitate in ethanol onto copper grids. The spectroscopic studies were performed by using a scanning electron microscopy (SEM, JSM.6300). The pH of the zero point charge (pHzpc) was determined by placing 1 g of cuttlefish bone into 250 mL glass stopper bottle containing 100 mL of 0.01 M NaCl solutions. The initial pH of these solutions was adjusted to 5.5, 6.5, 7.5, 8.5, 9.5, 10.5 and 11.5 by either adding 0.1 M NaOH or 0.1 M HCl. The bottles were then placed in the incubator shaker at 30 °C for 48 h, and the final pH of supernatant measured.

The ΔpH = (pH (final) - pH (initial)) was plotted against the initial pH, the pH at which ΔpH was zero was taken as a pHzpc.

Table 1: Physico-chemical characteristics [27]

Carbamazépine				
Chemical formula	**Class**	**Water solubility ($mg.l^{-1}$) at 25 ° C**	**pKa (20°C)**	**Molecular weight ($g.mol^{-1}$)**
C15-H12-N2-O	Anti-épileptique	17,7	13.9	236,27 $g.mol^{-1}$
Molecular structure 				

2.1.1. Adsorption experiments

All the adsorption experiments were carried out at 20°C by batch technique. Distilled water was used in preparing the stock solution of the test reagent (1000 mg/L) by dissolving a known quantity of Carbamazépine (CBZ). The pH of the initial Carbamazépine (CBZ) solutions was adjusted using known normal HCl (0.1M) and NaOH (0.1M). Individual batch adsorption experiments were carried out by shaking 25mg of cuttlefish bones with 25mL of known concentration of aqueous Carbamazépine (CBZ) at the Constant agitation speed (250rpm) for 1 h was maintained in individual adsorption processes. The effect of pH on the adsorption of Carbamazépine (CBZ) was studied by varying pH from 4.0 to14.

2.2. Adsorption isotherm

In order to identify the mechanism of the adsorption process, the adsorption isotherm values were evaluated and analyzed. Different isotherm models are available in the literature. Simple, reliable, and widely used models, such as linear, Langmuir, and Freundlich isotherms, were used in this present study. The chosen isotherm models were applied to establish the relationship between the amount of Carbamazépine (CBZ) adsorbed by the cuttlefish bones and its equilibrium concentration in the aqueous solution. The equilibrium studies were carried out using 25mg of cuttlefish bones in 25mL of Carbamazépine aqueous at different concentrations. The sorption capacity of the bones were evaluated by the amount of Carbamazépine (CBZ) aqueous adsorbed using the following expression.

$$Q = (C0 - Ce).V/M \quad (1)$$

where, Q (mg g^{-1}) is the amount of metal ions sorbed per gram of sorbent, C_0 and C_e are the initial and equilibrium concentrations of Carbamazépine in the solution (mgL^{-1}), M is the amount of sorbent (g), and V is the volume of the solution (L). The percentage of the Carbamazépine was evaluated as follows:

$$R\ \% = (C_0 - C_e).100/C_0 \quad (2)$$

The Langmuir model assumes that the adsorbent surface is homogeneous and contains only one type of binding site, so the energy of adsorption is constant, which is presented by the following equation.

$$Qe = (KL * Ce * q0) / (1 + Ce * KL) \quad (3)$$

The linear form of Langmuir adsorption isotherm can be expressed as follows:

$$(C_e/q_e) = 1/(q_0 K_L) + (1/q_0) * C_e \quad (4)$$

where q_o (mg g^{-1}) is the Langmuir constant related to the maximum monolayer adsorption capacity and K_L (L mg^{-1}) is the constant related to the free energy or net enthalpy of the adsorption. [28]

The Freundlich model can be applied for multilayer adsorption on a heterogeneous adsorbent surface, with sites that have different energies of adsorption. The Freundlich model is given by the following equation [29].

$$Qe = K_F * C_e^{1/n} \quad (5)$$

This expression can be linearized to give the following equation:

$$Ln\ Qe = \ln K_F + (1/n) \ln C_e \quad (6)$$

Where "K_F" (mg g^{-1}) and "n" are Freundlich constants related to adsorption capacity and intensity, respectively.

2.2.1. Adsorption kinetics:

Kinetic models are helpful in understanding the mechanism of molecule adsorption and in evaluating the performance of the adsorbents. A number of kinetic models have been developed to describe the kinetics of heavy molecule adsorption. In this present study, the kinetics of Carbamazépine adsorption on the cuttle bones was determined with different kinetic models such as. The effect of contact time was determined by the 'limited bath' technique.25mg cuttle bones are brought into contact with 25 mL of an aqueous solution of (CBZ). The solutions are in agitation using a mechanical stirrer for a time interval [0min to120 min]. Whenever varies in time we take a sample and make it past the centrifuge. Finally the supernatant was analyzed by UV spectrometer wavelength λmax = 271 nm.

The first-order rate equation of the Lagergren is one of the most widely used kinetic models for the adsorption of solute from a solution. [30] The model has the following form

$$(dQ/dt) = K_1 (Q_e - Q_t) \quad (7)$$

where Qe (mg g^{-1}) is the amount of the metal ions adsorbed on the adsorbent at equilibrium, and K_1 (min^{-1}) is the rate constant of the first-order adsorption. After integration and the application of boundary conditions $Q_t=0$ at t = 0 and $Q_t = Q_t$ at
t = t, the integral form of Eqn (7) becomes

$$Ln (Q_e - Q_t) = lnQ_e - K_1 t \quad (8)$$

The second-order kinetic model, on the basis of the adsorption equilibrium capacity, is as follows [31].

$$(dQ/dt) = K_2 (Q_e - Q_t)^2 \quad (9)$$

where K_2 (g mg^{-1} min^{-1}) is the rate constant of the second-order equation,
and q (mg g^{-1}) is the maximum dye adsorbed. After definite integration through the application of boundary conditions $Q_t=0$ at t = 0 and Qt = Q_t at t = t, Eqn (9) becomes the following

$$(t/ Q_t) = 1/ 2(Q_e^2 k_2) + t/Q_e \quad (10)$$

If the second-order kinetic model is applicable, then the plot of t/Qt versus t should give a straight line, and Qe and K_2 could be obtained from the slope and intercept of the straight line, respectively.

2.2.2. Sorption thermodynamics

Thermodynamic parameters, including changes in the free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) associated with the adsorption process, can be determined by using the following equations [32-33]

$$\Delta G = -RTLnKc \quad (11)$$

$$\Delta G = \Delta H - T\Delta S \quad (12)$$

The plot of ln Kc, as a function of 1/T, yields a straight line, from which ΔH and ΔS can be calculated from the slope and intercept, respectively.

3. Results and Discussion

4.3.1. Characterization of the sorbents

The X-ray diffraction (XRD) pattern shows that the cuttlefish bone has well crystallized form (Fig. 1) with a weak peak at 3.40A˚ which is characteristic of aragonite variety [34]. Also, the numerous peaks of CaCO3 on the right hand side of the spectrum were found to be moderately dominant, signifying the presence of a CaCO3 based structure [35]. Elemental analysis showed that the cuttlefish bone was 86% pure calcium carbonate CaCO3 with trace quantities of Na (8.275% as Na_2O), P (0.218% as P_2O_5), and Fe (1.128% as FeO_3). Cuttlefish bone had a very porous structure as shown in Fig. 2.a An EDX spectrum of CFPB shows the elements present in it and also the percentage composition of elements which is well depicted in
Fig 2.b.
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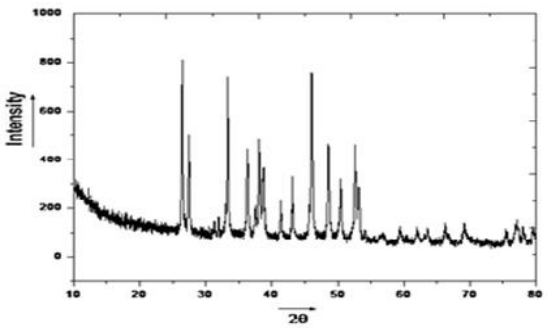

Figure 1: XRD patterns of cuttlebone particles

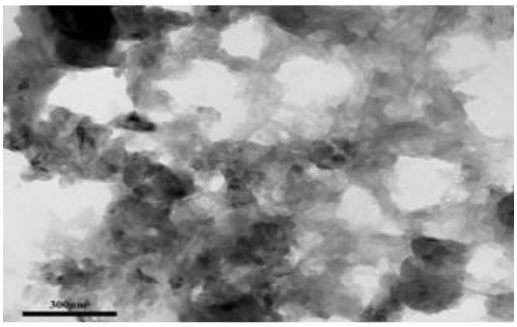

Figure 2a: (a).Transmission Electron Microscopy (TEM) of the cuttlefish bone.

Element	Weight %	Atomic %
NaK	1.3	2.3
K K	1.3	1.4
CaK	85.6	88.4
FeK	3.5	2.6
CuK	8.3	5.4
Total	100.0	100.0

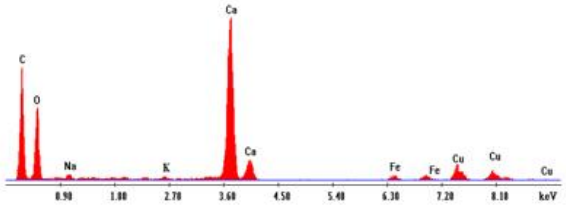

Figure 2b: EDAX spectra of CFBP

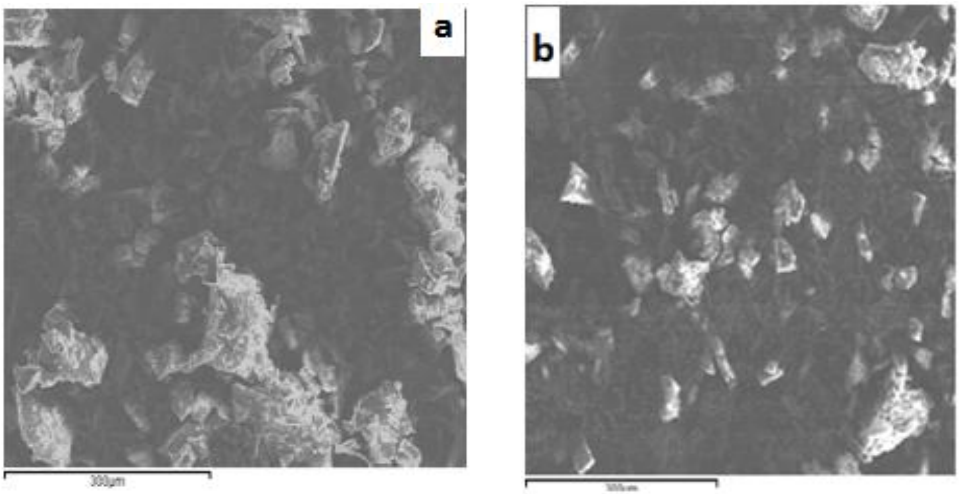

Figure 3: SEM images of CFBP and CFBP after adsorption of Carbamazépine.

The textural structural examination of CFPB and CFPB after the adsorption can be observed from the SEM photographs which are shown in Fig. 3. In Fig. 3a, CFPB showed a non-homogeneous and non-smooth surface which could easily absorb Carbamazépine molecules.

Also, the surface change in the SEM photograph of the CFPB after adsorption of Carbamazépine indicates the structural changes in the sorbent which is depicted in Fig. 3b

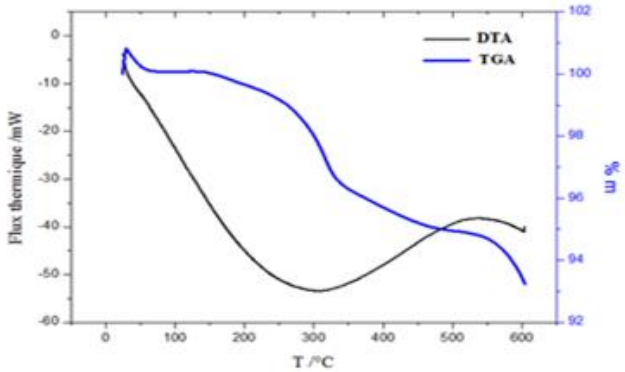

Figure 4: DTA-TGA Thermo grams of cuttlebone

Cuttlebone was composed of CaCO3 of 86%, which were determined by TGA-DTA cruves. The thermogrammes of cuttlebone particles is shown in Fig. 3. The degradation of cuttlebone occurred in two steps. In the first step, the decomposition of organic material took place at 300 °C followed by à pic endothèrmique with a weight loss of 5% in the second step, the decrease at 550°C. This decrease is ascribed to the burning of CaCO3 to produce calcium oxide (CaO) and carbon dioxide (CO2). The specific surface area of the crushed cuttlefish bone was found to be 5.6 m^2 g^{-1}. The experimental pHzpc of the cuttlefish bone is 9.8 (Fig. 6), which agrees closely with the experimental value of calcite determined by Somasundaran and Agar [36].

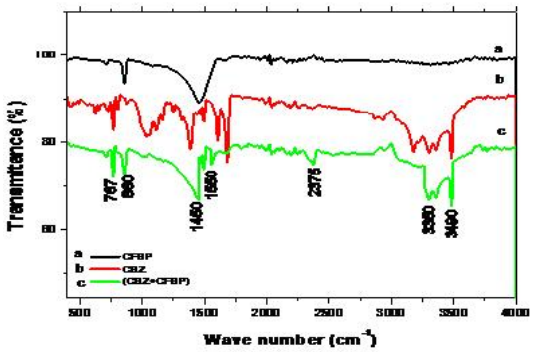

Figure 5: FT-IR spectra of (a) CFBP; (b) CBZ and (c) CFBP/CBZ.

A broad band at 1467 cm^{-1} indicates the presence of carbonate present in CFBP [37]. Several peaks related to CBZ are observed in Fig. 1b. The broad band centred at 3350–3500 cm^{-1} is likely due to the vibration of the amide form -CO-NH2. The peaks at 1600–1680 cm^{-1} are assigned to vibrations of hydroxyl groups. In the Fig. 1c, a band at 1450 cm^{-1} and at 860 cm^{-1} showing the presence of carbonates corresponding to CFBP present in the mixture of CFBP/CBZ. The peaks in the range of 3350 cm^{-1} and 3500 cm^{-1} indicate the presence of aliphatic N–H stretching. Also, a band at 2375 cm^{-1} corresponds C-H aromatic.

4.3.2. Effect of contact time

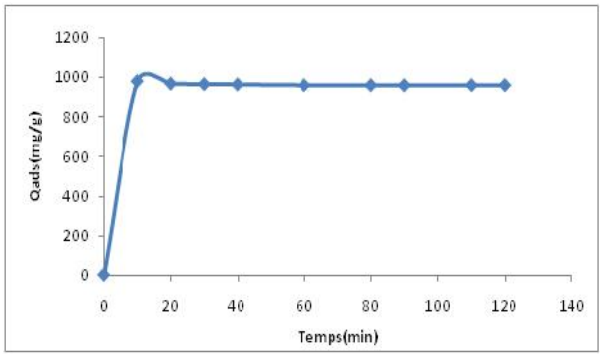

Figure 6: Effect of time on the adsorption of CBZ by cuttlefish bone (T = 25 ° C, pH = 9).

Figure 6 shows carbamazépine removal at different contact times using cuttlefish bone as an adsorbent. With increasing contact time, carbamazépine removal increased rather rapidly, but then gradually approached a more or less constant value denoting attainment of equilibrium. The sorption reaction may be considered to be occurring in three distinct phases. First, the initial rapid phase in which the rate of molecule CBZ removal was very rapid in less than 10 min. The fast kinetics of adsorption during the first minutes of the reaction, can be interpreted by the fact that at the beginning of adsorption, the number of available active sites on the surface of the adsorbent material, is much greater than that remaining after sites a certain time [38-39] en addition a specific chemical interaction (or affinity) and to diffusion and other driving forces. In the second phase, the sorption rate decreased due to less sorption as a result of the migration of carbamazépine cation layer to the interior pore/capillary surfaces. In the last phase, i.e., after 60 min, carbamazépine removal rate leveled of equilibrium and the non-availability of sorption sites significantly, denoting attainment of equilibrium and the non-availability of sorption sites.

4.3.3. Modeling of adsorption isotherm

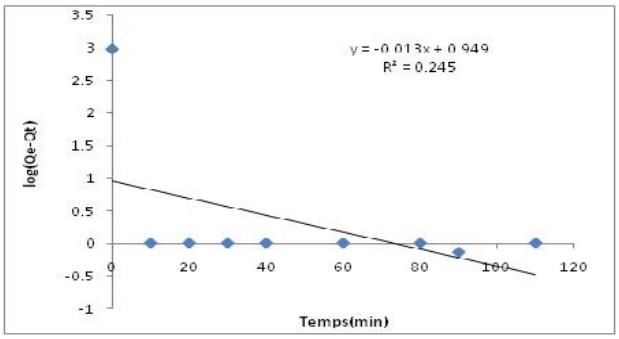

Figure 7: First order model kinetic model

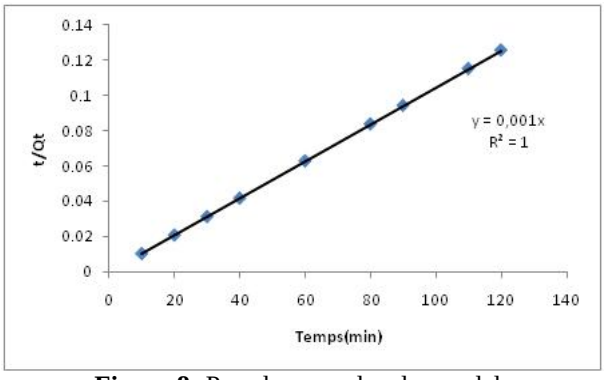

Figure 8: Pseudo second-order model

According to the results shown in Tables 1, we note that the pseudo second order model is the most reliable way to determine the order of adsorption kinetics of carbamazepine cuttlefish bone, which is a good correlation coefficient (R_2 = 0.99). Well and after values qe shown in Table 1, we note that calculated by the model of pseudo second order value is very close to that determined `expréimentalement that have justified the adsorption kinetics of carbamazepine used by cuttlebone is pseudo second order.

4.4. Adsorption isotherm

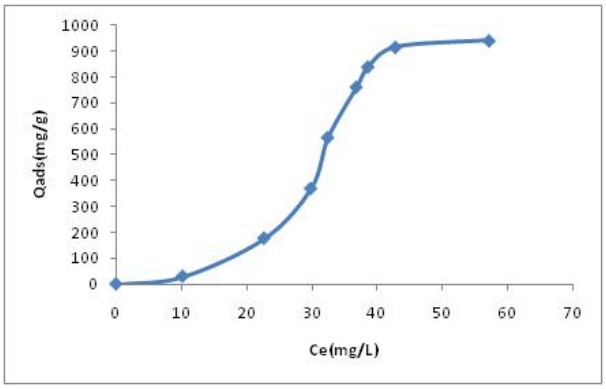

Figure 9: Adsorption isotherm on CBZ cuttlefish bone (pH =9, T = 25°C).

Fig. 9 shows the influence of the concentration in the ability of (CBZ) amount adsorbed which increases with the rise of equilibrium concentration. The equilibrium concentration of CBZ (Ce = 57, 27 mg / L) corresponds to a maximum adsorption capacity (Qe = 942 mg.g-1) in the concentration of range studied. The shape of the isotherm CBZ at pH 9 is S-type according to the classification of Giles et al. [40] Indeed, the isotherms of this class have at this low concentration, a concavity facing up, the adsorbed molecules promotes higher adsorption of other molecules. This is due to the interactions between the molecules which are attracted to Vander Waals forces. The maximum adsorption is (942 mg/g) CBZ is calculated per gram of cuttlefish bone.

4.4.1. Sorbent isotherms

The linear, Langmuir and Freundlich equations are commonly used in describing the adsorption equilibrium of wastewater treatment applications.

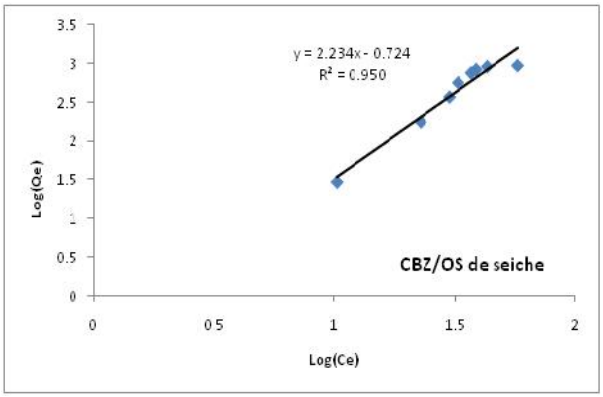

Figure 10: Freundlich isotherm model for the adsorption isotherms of CBZ on Cuttlebone (pH =9, T = 25° C).

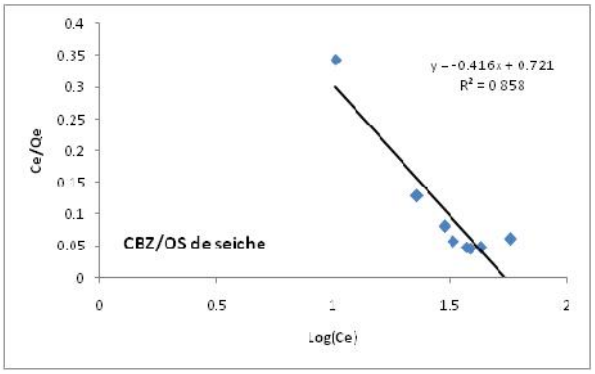

Figure 11: Langmuir isotherm model for the adsorption isotherms of CBZ on Cuttlebone (pH =9, T = 25° C).

Figs. 11 and 5 shows the Freundlich and Langmuir equation obtained by the adsorption of CBZ onto cuttlebone.
We note that the linearization of adsorption isotherms of carbamazepine cuttlebone is satisfactory with good coefficients correlation (Figure 11). We can say that the model is Freundlich adequate for a good description of the isothermes d'adsorption.

From Fig.12, we deduce that the Langmuir model is not suitable for modeling the adsorption isotherms carbamazepine cuttlebone throughout the concentration range.

4.4.2. Effect of pH

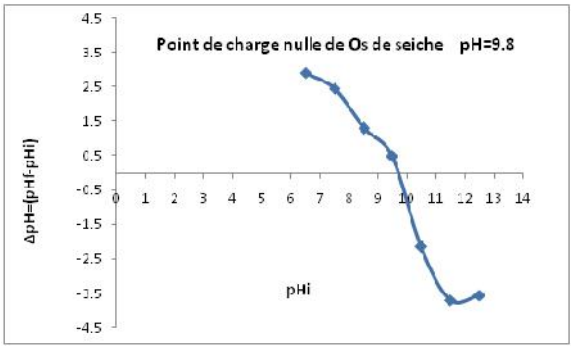

Figure 12: Zeta potential of cuttlefish bone.

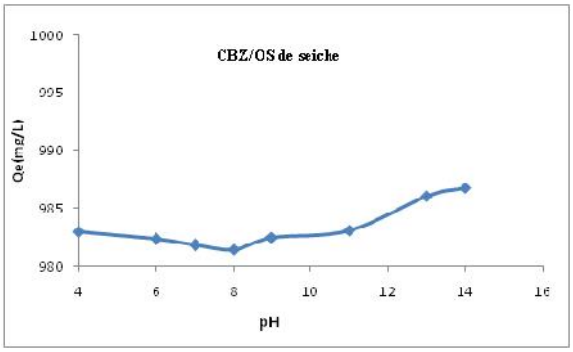

Figure 13: Effect of pH on the removal of carbamazépine(Carbamazépine initial concentration = 25 mg/l, T =25° C)

Fig. 13 shows the effect of pH on the removal of carbamazépine by sorption on the cuttlefish bone. As the pH of the Carbamazépine solution increased from 4 to 14.

When the solution is more basic than the point at zero charge (pH > pHzpc), negative species will predominate and the surface will be negatively charged leading to an increase in the amount of carbamazépine removed from the solution. Similarly, when the solution is more acidic than the point at zero charge (pH < pHzpc), positive species will predominate and the surface will be positively charged. A number of authors [41–45].CBZ molecules have pKa of 13.9 what we find on the Figure 15 or the absorption maxima are at pH 14, when pH = pKa, the acidic species takes their anionic form: electrostatic interactions are dominant.

Table 2: The parameters of kinetic model

First order kinetic model					Pseudo second-order kinetic model		
adsorbent	PPs	Qe (mg/g)	K_1 (min^{-1})	R^2	Qe (mg/g)	K_2 ($g.mg^{-1}min^{-1}$)	R^2
cuttlefish bone	CBZ	2.583	0.013	0.245	1000	0.01	0.99

Table 3: The parameters of Langmuir and Freundlich isotherms

	Langmuir parameters			Freundlich parameters		
cuttlefish bone/CBZ	K_L ($g.L^{-1}$)	q_0(mg/g)	R_2	K_F ($g.L^{-1}$)	n	R_2
	0.57	2.403	0.858	0.484	0.447	0.95

Table 4: Experimental results of thermodynamics of adsorption of CBZ.

Température K	**ΔH ° ($J.mol^{-1}$)**	**ΔS° ($J.mol^{-1}K^{-1}$)**	**ΔG° (J/mole)**
293	43.66	-10.73	3187 ,55
313	43.66	-10.73	3402,15
333	43.66	-10.73	3616.75
353	43.66	-10.73	3831.35

4.4.3. Effect of temperature

The influence of temperature was studied with CBZ solutions (25ml) equal to 1g. L^{-1} of concentrations and a pH equal to 9, immersed in a water bath to keep the temperature constant. The adsorbent (25 mg) was then added and we stir using a magnetic stirrer. We studied the Following adsorption temperatures: 20, 40, 60 and 80 ° C.

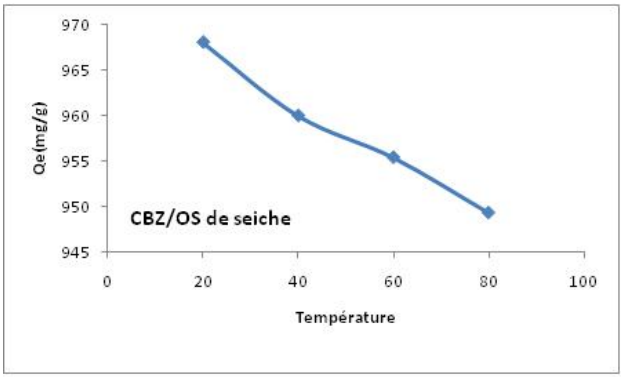

Figure 14: Effect of temperature on the adsorption of CBZ

We find that increasing the temperature from 20 to 80 ° C induces a decrease of the adsorption capacity. The temperature rise would affect destabilize the physical forces involved, we can conclude that there is an optimum value of temperature to promote the adsorption of CBZ.

In general, the adsorption is always accompanied by a thermal process [45, 46] which may be either exothermic (ΔH<0) or endothermic (ΔH>0). Measuring the heat of adsorption ΔH is the main criterion that differentiates the chimisorption of physisorption.

The heat of adsorption ΔH is given by the Gibbs-Helmholtz relationship [32, 33]:

$\Delta G = -RTLnKc$ (1) $\Delta G = \Delta H - T\Delta S$(2)

(2) / (1) $\Longrightarrow$ $LnK_c = \Delta S°/R - (\Delta H°/RT)$ With : $K_c = C_e/(C_o - C_e)$

Where:

Kc: Equilibrium constant

ΔG: Gibbs free energy (joule / mole)

ΔH: Enthalpy (joules / mole)

ΔS: Entropy (joule / mole.K)

T: absolute temperature (K)

Co: initial concentration of the adsorbate

Ce = equilibrium concentration of the adsorbate

R: gas constant (8.314 Joule / mol K)

The heat of adsorption ΔH and the entropy ΔS adsorbate on cuttlefish bones was determined graphically by plotting LnKc in function of the inverse of the temperature in degrees Kelvin of the medium as shown in the figure.

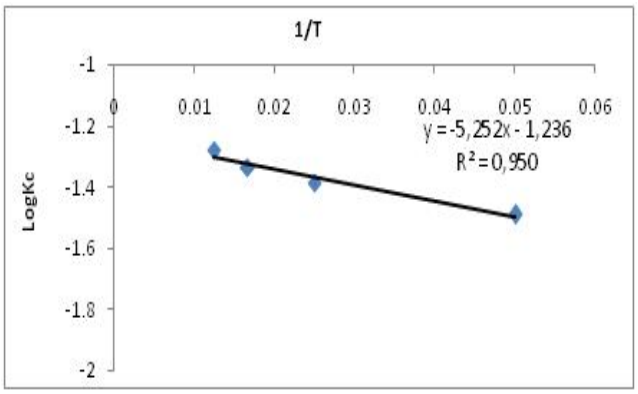

Figure 9: Determination of the enthalpies and entropies of adsorption of CBZ on Cuttlefish bone

The positive value of ΔH (43, 66J.mol^{-1}) confirms that the adsorption of adsorbate on the cuttlefish bone is an endothermic process. Low values of this heat (<40 KJoule mol) indicate that this is a physical adsorption. The negative value indicates that the entropy of adsorption of adsorbate on the cuttlefish bone is accompanied by a disorder of the medium. ΔG ° values increase with temperature, showing spontaneity in the sorption process of CBZ reagent on cuttlefish bone. The adsorption process is thermodynamically possible at room temperature.

4. Conclusion

Elemental analysis showed that cuttlefish bone was 86% pure calcium carbonate. X-ray diffraction pattern, TEM and SEM studies reveal that cuttlefish bone is well crystallized, uniform and porous structured. The maximum percentage of Carbamazépine removal was found to be 94 % using CFPB at 60 min. The kinetic data of carbamazépine followed the pseudo second-order kinetic model, with a qe value of 1000 (mg.g^{-1}). The adsorption isotherms Carbamazépine by cuttlefish bone are described satisfactorily by the Freundlich model. The positive value of ΔH^o confirmed the endothermic nature of adsorption. The negative value indicates that the entropy of the absorption of adsorbate on the cuttlefish bone is accompanied by a disorder of the medium. ΔG ° values increase with temperature, showing spontaneity in the sorption process of CBZ reagent on cuttlefish bone. The adsorption process is thermodynamically possible at room temperature.

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