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Adsorption Kinetics Study of Bisphenol-A in Aqueous Solution on Clay Materials

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A B S T R A C T

The problem of the elimination of bisphenol A from aquatic environments by low-cost, efficient and accessible processes is a major problem for water treatment specialists, especially in developing countries. Many studies have investigated the adsorption of certain endocrine disruptors on materials such as activated carbon and zeolite. However, the use of clays remains rare. The objective of this study is to evaluate the adsorption capacity of bisphenol A on two types of clay balls from Daloa and Korhogo ; two localities in the Ivory Coast. The balls were fabricated from clay powders of diameter between 45 and 125 µm. The balls of clay obtained, of diameter 5mm, were dried before being calcined at 550°C in a Naberthern muffle furnace. The specific surface area and the pH of zero charge were determined by analytical methods. The influence of contact time adsorbent-adsorbate, initial concentration and pH of the bisphenol A solution on adsorption was studied, in batch mode, in order to determine the best conditions for removal of the pollutant. The determination of residual concentrations was carried out with a JENWAY 6850 UV-Visible spectrophotometer. The adsorption results showed that after 4 hours, the elimination of bisphenol A was maximal with a yield of 92.99%, at pH 9, for the Daloa clay. For the Korhogo clay, a removal yield of 69.03% is observed at pH 4, after 5 hours of contact time. It is also noted that the pseudo-second order kinetic model describes correctly the adsorption of bisphenol A on the two materials. These results indicate that the bisphenol A can be effectively removed by the balls elaborated from Ivory Coast clays.

Introduction

Endocrine disruptors are enormous nuisances to human and animal health, as they are capable of inducing abnormalities in endocrine functions in wildlife and humans at concentrations in the microgram per liter range (Ruaux, 2019). Among these disruptors, bisphenol A is used in excess in the industrial manufacture of polycarbonate-type plastics and epoxy resins. It can cause diseases such as epimutagenic, obesogenic, diabetogenic and endometriosis, vitellogenin in humans and animals (Anger and Kintz, 2011). This situation is of concern for developing countries such as Côte

d'Ivoire where there is a lack of knowledge about the state of contamination of aquatic ecosystems by this type of contaminants. Moreover, to date, very few studies have been conducted on the presence of bisphenols in the aquatic systems of Côte d'Ivoire. However, the risk is very real. In fact, several used items likely to contain these compounds are drained into water bodies on a daily basis. Consequently, it is imperative to take an interest in the quality of these waters, thus becoming a public health concern.

The treatment of water containing this type of dye is of great interest (Alexander *et al.*, 1998; Söffker *et al.*, 2012; Tijani *et al.*, 2013). In this perspective, several depollution processes such as adsorption, chemical oxidation, photo degradation have been implemented. These techniques are very effective, but their high cost has led many researchers to seek other less expensive and abundant materials such as clays (Liu *et al.*, 2009; Lee *et al.*, 2004). The importance given to these materials is due to their availability in nature and their high retention capacity favored by their layered structure which gives them a large specific surface area (Nandi *et al.*, 2009). Several works carried out on clays have shown their effectiveness for the treatment of contaminated water (Gueu *et al.*, 2019). The aim of this work is to evaluate the adsorption capacity of bisphenol A (BPA) on two types of local clays in order to assess their performance, by examining the effect of operating parameters such as contact time, initial bisphenol A concentration and pH of the solution on adsorption.

Materials and Methods

The raw clays used in this work are clays taken from two cities in Ivory Coast (Daloa and Korhogo). The bisphenol (BPA), of raw formula is $C_{15}H_{16}O_2$ and is supplied by the company Fluka with a purity of 99%. All chemicals used are 98% pure or higher.

Production of clay balls

Raw clays are crushed and sieved to obtain fractions of diameter D (45 µm ≤ D≤125 µm). A mass of 100 g of each raw clay is weighed and placed in various porcelain mortars. A volume of 40 mL of distilled water is added and mixed until a homogeneous and consistent paste is obtained for each clay. Then, beads with a diameter of 0.5 cm and a mass between 0.14 g and 0.20 g are made by hand from this clay paste. Finally, the obtained clay beads are dried in an oven at 60 °C for 48 hours, then fired in the oven at 550 °C for 2 hours.

Characterization of beads

Specific surface area

A mass of 0.5 g of each raw clay is mixed with a reactor with 40 mL of a hydrochloric acid solution (0.1 M). The volume is then made up to 50 mL with distilled water, after adjustment of the pH to 3, 10 g of NaCl is added, followed by a dosage with a solution of NaOH (0.1 M) up to pH 4, and finally the pH of the solution is adjusted to pH 9. The formula (1) is used to determine the specific surface area of the clays.

$$S(\mathrm{m}^2.\mathrm{g}^{-1}) = (32 \times \mathrm{V}) - 25 \quad (1)$$

NB: The volume of NaOH that allowed the passage from pH = 4 to pH = 9 is noted V.

Zero-point pH charge (pH_{PZC})

Its determination consists of adjusting the pH values to 3, 5, 7, 9 and 11 in different beakers containing 20 mL distilled water. A mass of 0.1 g clay powder was subsequently added. The mixture was stirred for 24 hours and then the pH value was measured after the reaction time had elapsed. The zero-charge point is obtained by plotting the curve C (ΔpH= f(pHi)), the pH value pH_{PZC} is given by the intersection of this curve with the abscissa axis (y = 0).

Adsorption experiments

Adsorption experiments were carried out in batch. The clay beads were placed in mini amber reactors containing the bisphenol A solution.

Influence of contact time

A mass of 1 g of adsorbate is brought into contact with 10 mL volumes of BPA solution in the reactors. The mass was stirred and samples were taken at defined time intervals. These samples were analyzed by spectrophotometry (UV/Visible JENWAY 6850) at the maximum wavelength of 276 nm. The amount adsorbed and the adsorption rate were calculated according to equations (2) and (3).

$$Q_t = \frac{((C_i - C_r) \times V)}{m} \quad (2)$$

$$\text{Adsorption rate } (\%) = \frac{(C_i - C_r)}{C_i} \times 100 \quad (3)$$

With:

Qt: quantity of pollutant per unit mass of clay (in mg/g)

Ci: Initial concentration of Bisphenol A (mg/L)

Cr: residual concentration at equilibrium (mg/L)

V: volume of Bisphenol A solution (L)

m: mass of the clay (g)

Influence of the initial concentration of the solution

The effect of the initial concentration of BPA was studied by mixing with 10 mL of BPA solution at concentrations of 3, 5, 10 and 15 mg/L. This was agitated at room temperature and at the pH of the solution.

Influence of pH

A mass of 1 g of clay beads by mixing with 10 mL of BPA solution at a concentration of 5 mg/L and at room temperature. The pH of the solution was adjusted to the following different values (4, 6, 8, 9, 10 and 12) using NaOH (0.1 N) and HCl (0.1 N) solutions.

Modeling of adsorption kinetics

In order to study the adsorption mechanism, pseudo-first order and pseudo-second order kinetic models were used to test the experimental data.

Pseudo-first order model

The pseudo-first-order model is expressed according to the following formula (Önal *et al.*, 2007).

$$\log(Q_e - Q_t) = \log Q_e - \frac{K_1}{2.303} t \quad (4)$$

With:

Q_e: quantities adsorbed at equilibrium

Q_t: quantities adsorbed at time t

K_1: speed constant

Pseudo-second order model

The kinetic model of the pseudo-second order is expressed as follows (Ho and Mckay, 1999).

$$Q_t = \frac{(K_2 \times t \times Q_e)}{(1 + K_2 \times Q_e)} \quad (5)$$

The integration between 0 and t for time and 0 and Qt for the adsorbed quantity leads to *t*.

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (6)$$

K_2 is the pseudo-second order velocity constant ($mg.g^{-1}.min^{-1}$)

Results and Discussion

Production of balls

The preparation of the clays resulted in balls. figure 1 is an illustration of the gross and prepared clay balls by calcination at 550°C.

Characterization of clays

Table 1 gives the measured characteristics of Daloa and Korhogo clays.

As shown in the table, the specific surface areas of the calcined clays of Daloa and Korhogo are much larger than those of the raw clays. This shows that the calcination of the clays at 550°C creates a large pore opening resulting in an increase in specific surface area (Ely, 2010).

The pH zero charge for Daloa clay is 9.8 and that of Korhogo clay is 6.7 which means that at these pH values the surface charge of the clays is zero. Thus, at pH values below the pH_{PZC} of each clay, the surface of the clay is positively charged and otherwise the surface is negatively charged (Zahaf, 2017).

Effect of contact time

Figure 2 shows the contact time study. Indeed, this Figure represents the curves of evolution of the BPA adsorption rate versus contact time at the initial concentration of 5 mg/L for the Daloa and Korhogo clay beads. The curves show that the process of BPA adsorption takes place in two phases. The first, rapid, could be explained by the abundance and availability of adsorption sites on the surface of adsorbent allowing a rapid fixation of the adsorbate. The slow phase could be due to the diffusion process through less accessible sites before reaching an adsorption equilibrium where all the sites are occupied. It could also concern adsorption sites of lower affinity or not directly accessible to bisphenol A molecules. These results are supported by those of studies conducted by Yang *et al.*, (2016) and Li *et al.*, (2015) for the adsorption of bisphenol A using montmorillonite and bentonite as adsorbents respectively. It is noted that equilibrium is reached after 300 min (5 h) and 200 min (4 h) respectively for Korhogo clay and Daloa clay with respectively 80.09% and 69.03%.

Effect of the initial concentration of the pollutant

The figure 3 shows the effect of the initial concentration of the solution on the adsorption of bisphenol A on clays from Daloa (aD) and Korhogo (aK).

This Figure 3 shows that for each type of clay considered, the adsorption rate increases with the concentration of BPA in solution and decreases after reaching a maximum. Maximum adsorption is observed at an initial concentration of 5 mg/L for both clay types. Adsorption rates are 79.59% for Daloa clay and 69.63% for Korhogo clay. This difference in removal efficiencies could be related to the specific surface areas of the clays and the physico-chemical properties of the clay-bisphenol A system formed between each type of clay and the adsorbate. The decrease in the adsorption rate beyond 5 mg/L could be explained by the fact that beyond this concentration the number of moles of BPA increases in solution while the number of adsorption sites is static. Similar results were observed for the adsorption of bisphenol A and 2,4-dichlorophenol on transition metal-modified clays (Ortiz-Martínez *et al.*, 2016).

Effect of the initial pH of the bisphenol A solution

The influence of the initial pH of the solution on the adsorption of BPA on clays from Daloa and Korhogo is illustrated in figure 4.

The representative curves of the two clays have different paces. For Daloa clay, an increase of 11.67% in the adsorption rate is observed when the pH goes from 4 to 9 before decreasing. While the BPA adsorption rate observed on Korhogo clay undergoes a gradual drop between 4 and 12; a drop of 25.93% from pH = 8 to pH = 12. These different variations in the adsorption rate on these clays could be related to the pH_{Pzc} of the clays and the ionic state of the BPA molecule as a function of pH.

Table.1 Specific surface area and pH of Daloa and Korhogo clays

Parameters	Gross specific surface area (m^2 / g)	Fired specific surface area (m^2 / g)	pHPZC
Clay from Daloa	93,4	289,2	9,8
Clay from Korhogo	74,2	234,2	6,7

Table.2 Kinetic parameters of the Korhogo and Daloa clays

	C_0 (mg/L)	Qe_{exp} (mg/g)	Pseudo first order models			Pseudo second order models		
			Qe_{cal} (mg/g)	k_1 (min^{-1})	R^2	Qe_{cal} (mg/g)	k_2 (min^{-1})	R^2
Clay from Daloa(aD)	3	0,02	0,16	0,01	0,77	0,02	1,11	0,99
	5	0,04	0,24	0,01	0,98	0,04	0,49	1,00
	10	0,08	0,30	0,01	0,88	0,07	0,67	1,00
	15	0,12	0,37	0,01	0,94	0,13	0,13	0,99
Clay from Korhogo (aK)	3	0,02	0,17	0,01	0,96	0,02	0,46	0,99
	5	0,03	0,22	0,01	0,99	0,04	0,27	0,99
	10	0,07	0,29	0,01	0,96	0,08	0,14	0,99
	15	0,10	0,35	0,01	0,99	0,12	0,10	1,00

Fig.1 Clay balls from Daloa (A) and Korhogo (B) calcined at 550°C.

Fig.2 Influence of the contact time on the adsorption of Bisphenol A (mass of each adsorbent= 1 g; concentration= 5 mg/L; ambient temperature T=25±2°C; pH of the solution pH= 5±02).

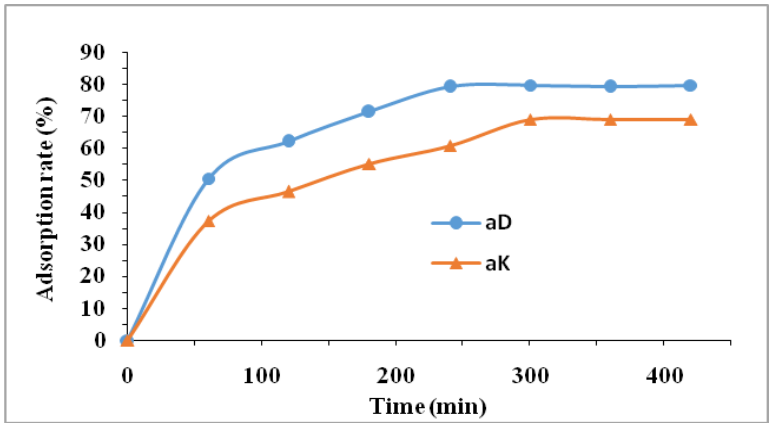


Fig.3 Evolution of adsorption rate as a function of the initial concentration of the pollutant (Mass aD=1 g; mass aK=1 g; equilibrium time aD= 4 hours; equilibrium time aK= 5 hours, pH of the solution pH=5±02; ambient temperature T=25±2°)

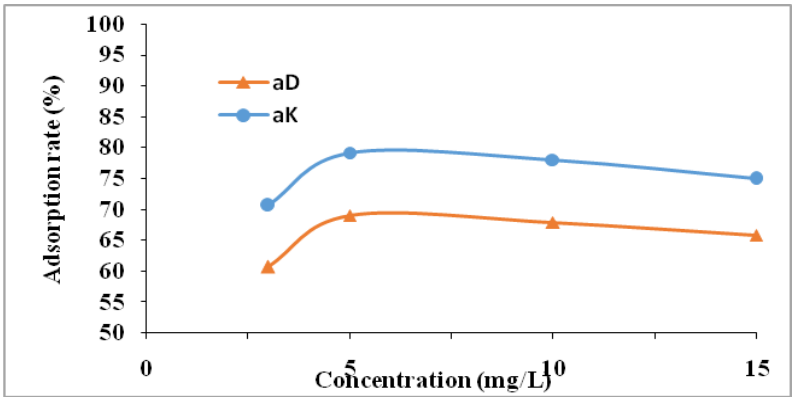


Fig.4 Evolution of the adsorption adsorption rate as a function of the initial pH of the solution (Mass aD m=1 g; mass aK m=1 g; equilibrium time aD t1= 04 hours and equilibrium time aK t2= 05 hours; solution concentration Co=05mg/L and ambient temperature)

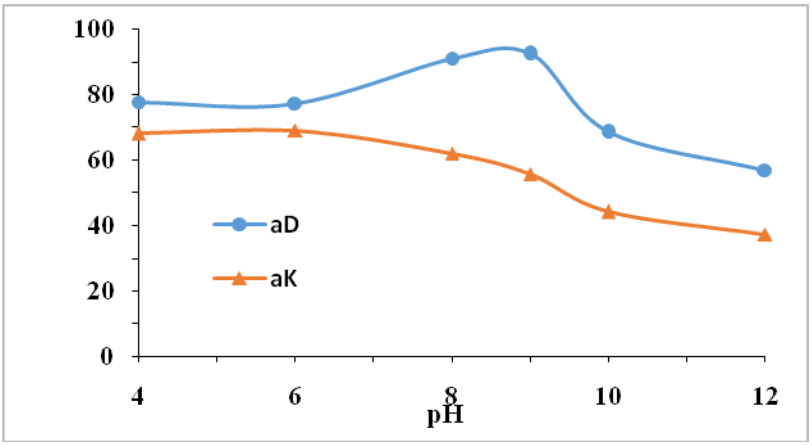
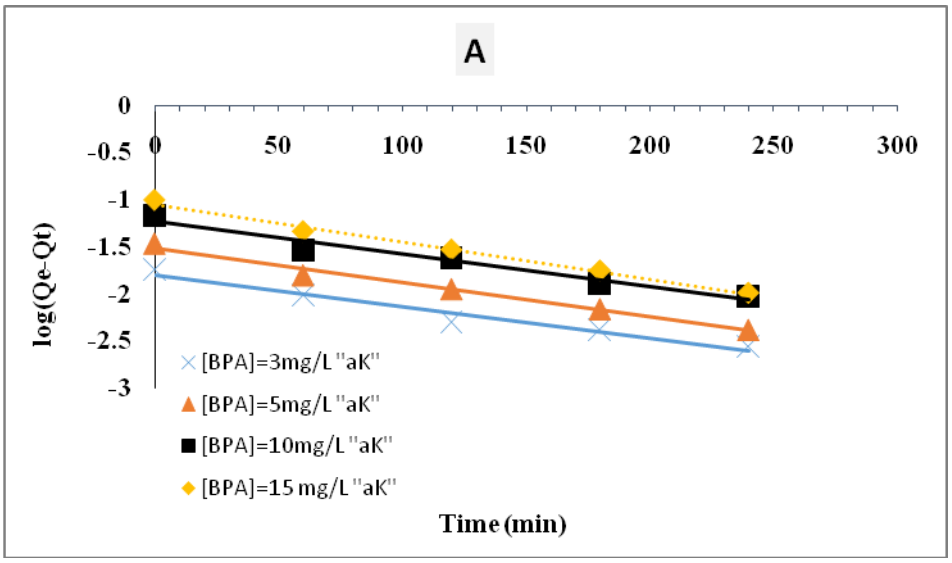


Fig.5 Pseudo first order kinetic models of the Korhogo (A) and Daloa (B) clays



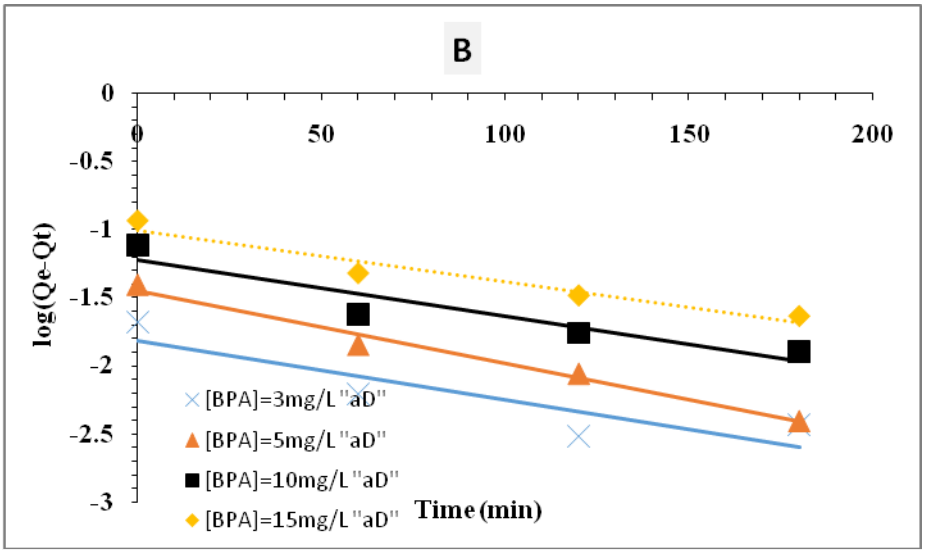
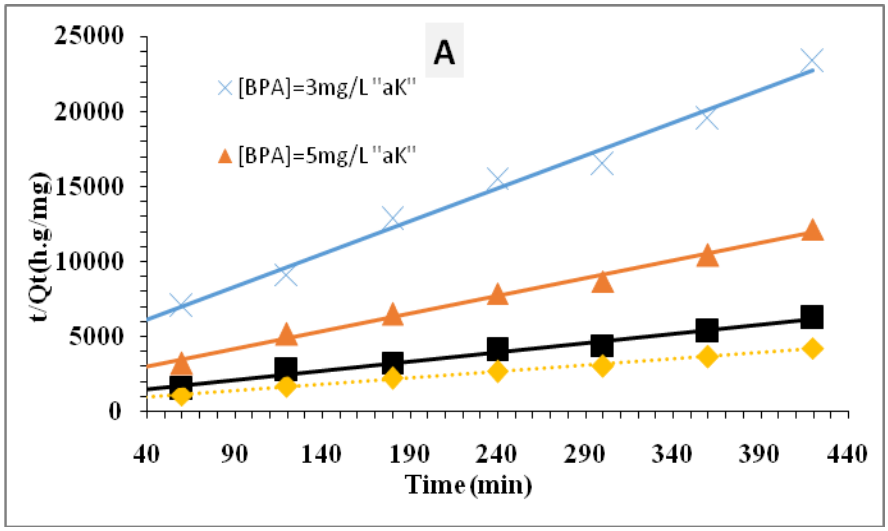
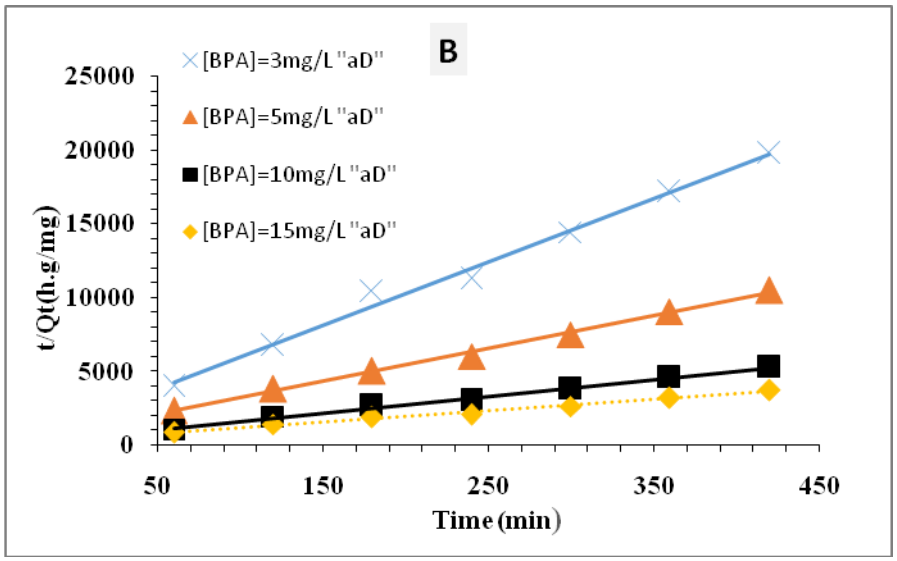


Fig.6 Pseudo second order kinetic models of the Korhogo (A) and Daloa (B) clays





The zero-point charge pH of the raw Daloa and Korhogo clays being 9.8 and 6.7 respectively; the decrease in the adsorption rate may be due to the fact that the surface of the clay is negatively charged at pH >pH_Pzc, and that the bisphenol A molecules in solution are in the neutral form, BPA^- and BPA^{2-} then there is repulsion.

On the other hand, at pH values <pH_Pzc, the surface of the clay is positively charged, and therefore likely to adsorb adsorption bisphenol A anions because there is attraction and therefore an increase in the adsorption rate. The work of Guo *et al.*, (2011), Peng *et al.*, (2015) and Qiu *et al.*, (2016) on bisphenol A removal has reached the same conclusion.

Kinetics Study

Bisphenol A adsorption kinetics were studied at optimal parameters at different initial concentrations (3 mg/L, 5 mg/L,10 mg/L and 15 mg/L) for each type of aD and aK clays. The pseudo-order 1 and order 2 kinetic models of the two clays are shown in Figures 5 and 6.

Figures 5 and 6 reveal that the representation of the pseudo second order models (Figure 6) gives a better linearity than those of the pseudo first order models (Figure 5). The equilibrium adsorbed quantities and coefficients of determination calculated for the two kinetic models are presented in Table 2.

From Table 1 it is clear that the adsorption kinetics of bisphenol A by Daloa and Korhogo clay is of pseudo second order. This result assumes that the adsorption rate is proportional to the square of the number of unused adsorption sites. Similar results were observed by Yang *et al.*, (2016).

The objective of this study was to evaluate the adsorption capacity of bisphenol A on two types of clay beads from the cities of Daloa and Korhogo. The characteristic study showed that the Daloa clay beads have a higher specific surface area than those from Korhogo. The use of Daloa and Korhogo clay for the removal of bisphenol A from synthetic waters gave very satisfactory results, 92.99% and 69.03% respectively. These results show that the adsorption of bisphenol A is influenced by several factors including pH (pH = 9 (aD) and pH = 6 (aK)). The application of kinetic models to the bisphenol A adsorbent system showed that, the pseudo-second order kinetic model applies best regardless of the type of clay used. Overall, these results lead to the conclusion that bisphenol A can be efficiently removed by clay beads, especially those of Daloa.

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