Adsorption of Atrazine from Aqueous Solution onto Peanut Shell Activated Carbon: Kinetics and Isotherms Studies

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Abstract: In this study, the activated carbon (AC) was prepared from phosphoric acid activation of peanut shell and used as adsorbent for atrazine removal from aqueous solutions. The prepared AC was characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) techniques. The effect of parameters such as solution pH, contact time, adsorbent dosage and concentration of atrazine solution were studied on adsorption process. The results of characteristics study shown that the surface of AC was porous with numerous functional groups. The kinetic results revealed that the adsorption process was well described by the pseudo-second-order model than the pseudo-first-order model. The intraparticle diffusion model involved in the adsorption process by multi steps. The equilibrium data were in the best agreement with the Langmuir model than the Freundlich and the Temkin models. The maximum adsorption capacities calculated according to the Langmuir isotherm were 66.66, 52.63 and 48.08 mg g⁻¹ at 30°C and at pH 5, 7 and 9 respectively. The results of this study pointed out that the activated carbon prepared from the peanut shell has strong adsorption potential toward the atrazine herbicide, hence, it could be used for efficient adsorption of pesticide residues and other hazardous pollutants from wastewater.

Keywords: Peanut Shell, Activated Carbon, Atrazine, Adsorption

1. Introduction

In most of West African countries, the agriculture has been modernized since last decades. Using of phytosanitary by-products has led to an increase in agricultural yields through the fight against weeds and harmful insects [1]. Atrazine is one of the most widely used herbicides in agricultural applications. However, atrazine has also negative effects on the environment and on human health, because it is classified as carcinogenic and mutagenic compound [2]. Atrazine residues were also found in the treated soils and surface water [3]. Thus, several methods such as oxidation [4], photocatalysis [5], electrochemical [6] and adsorption [7] are used for herbicide residues removal from polluted water. Among these methods, adsorption is widely used because of its low-cost and easily application. The adsorbents mostly used are activated carbon [7, 8], graphene oxide [9], nanocomposite material [10] and others non-conventional absorbents such as Moringa oleifera seeds and tree fern [11-13]. Activated carbon is mainly used as adsorbent because it presents large specific surface area and numerous pores. However, the commercial activated carbon has high cost and is difficult to regenerate. Thus, several studies have reported the development of activated carbon from agricultural waste such as date seed shells [8] and peanut husk [14]. Furthermore, in Benin, the peanut shells are abandoned in household garbage, which cause the environmental pollution. In addition, our previous work has revealed that the activated carbon obtained from peanut shells has shown high adsorption property for 2,4-dichlorophenoxyacetic pesticide [15]. This study investigates the use of activated carbon from
peanut shells for efficient removing of atrazine from water. The prepared activated carbon was characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Then, the application of activated carbon for atrazine removal from aqueous solution in a batch mode was evaluated. The effects of solution pH, concentration of adsorbate, adsorbent dose and contact time were studied. Kinetics and isotherms studies were also performed to explain the mechanism of adsorption process.

2. Materials and Methods

2.1. Reagents

H₃PO₄ (85%, d = 1.71), HCl (36%, d = 1.18), CH₃OH (95%) and NaOH were supplied from Sigma Aldrich Spain. Atrazine (C₁₂H₁₄ClN₃, 80%) was supplied by Baochen Chemical Industry, China. Peanut shells were collected from women's cooperative groups in Kouande town, Benin. For the adsorption experiments a stock solution of 500 mg L⁻¹ of atrazine was prepared by dissolving 312.5 mg of atrazine in 500 mL of methanol. The atrazine solution with concentration range 10 - 100 mg L⁻¹ were obtained by dilution with distilled water of the stock solution.

2.2. Preparation of Activated Carbon

The activated carbon was prepared according to our previous work [15]. The dried peanut shells (0.8 and 1 mm) were mixed with 30% H₃PO₄ in impregnation ratio 1:3 (weight of peanut shells/weight H₃PO₄). The obtained mixture was heated at reflux for 2 h and then dried at 60°C for 24 h. The resulting residue was carbonized in a muffle furnace (Carbolite Scientific) at 450°C for 3 h with 10°C/min of heating rate. The activated carbon obtained was washed several times with distilled water until neutral pH, dried at 110°C for 12 h and then sieved before used as adsorbent.

2.3. Characterization of Activated Carbon

Activated carbon (AC) was characterized using FTIR and SEM methods. The characteristics of the surface functional groups of the adsorbent were determined with Fourier transform infrared spectroscopy (FTIR) using Perkin Elmer 100 Series spectrometer. The morphology of the adsorbent surface was characterized using scanning electron microscopy (SEM-FEG 1540XB).

2.4. Batch Adsorption

2.4.1. Experimental Procedure

The adsorption experiments in batch system were carried out with 50 mL of 50 mg/L atrazine solution. The initial pH of the solution was adjusted at 5 with 0.10 M HCl and 0.10 M NaOH solutions. An amount of 0.05 g of AC was introduced into the solution and the mixture was stirred at 100 rpm for 2 h and then filtered through Whatman N°1 filter paper. Final concentrations of atrazine in the filtrates were quantified by measurement of the absorbance of filtrate at 221 nm wavelength using UV-Vis spectrophotometer (VWR 1600 PC). The effects of solution pH (2.0-10.0), adsorbent dose (0.01 - 0.10 g), atrazine concentration (10-100 mg L⁻¹) and contact time (0 - 120 min) were studied on the adsorption process. The adsorption capacity qₑ (mg/g) of AC and the removal percentage of atrazine (RE%) were calculated using the following expressions:

\[ qₑ = \frac{(C₀−Cₑ)V}{W} \]  
\[ RE(\%) = \frac{100(C₀−Cₑ)}{C₀} \]

where Co and Ct (mg/L) are the initial and final concentration of atrazine respectively, V (L) is the volume of the atrazine solution and W (g) is the weight of AC used.

2.4.2. Kinetic Study

The study of adsorption kinetic was performed using pseudo-first-order [16], pseudo-second- order [17] and intraparticle diffusion [18] models. The expressions of kinetic models are presented as follows:

Pseudo-first-order:  \[ ln(qₑ - qₜ) = ln(qₑ - k₁t) \]

Pseudo-second-order:  \[ \frac{t}{qₜ} = \frac{1}{k₂qₑ²} + \frac{1}{qₑ}t \]

Intraparticle diffusion:  \[ qₜ = k_{id}t^{1/2} + C \]

where qₑ and qₜ (mg g⁻¹) are the adsorption capacities at time t and at equilibrium respectively, k₁ (min⁻¹) is the rate constant of the pseudo-first-order model, k₂ (mg g⁻¹ min⁻¹) is the rate constant of the pseudo-second-order model, k_{id} (mg g⁻¹ min⁻¹/2) is the rate constant of the intraparticle diffusion model, C (mg g⁻¹) is the intercept related to the boundary layer effect and t is the contact time (min).

2.4.3. Adsorption Equilibrium Isotherms

The equilibrium data were described using the Langmuir [19], Freundlich [20] and Temkin [21] isotherms. The linear forms of isotherms are written as follows:

Langmuir:  \[ \frac{Cₑ}{qₑ} = \frac{1}{qₘK_L} + \frac{Cₑ}{qₘ} \]

Freundlich:  \[ lnqₑ = ln K_f + \frac{1}{n} ln Cₑ \]

Temkin:  \[ qₑ = B lnA_T + \frac{B lnCₑ}{T} \]

where qₑ (mg/g) is the maximum adsorption capacity, K_L (L/mg) is the constant of the Langmuir isotherm, K_f (mg/g (L/mg)¹) and n are the parameters of the Freundlich model, R = 8.31 J/K/mol is the gas constant, T (K) is the absolute temperature, b₁ (J mol⁻¹), A_T (L/mg) and B (B = \frac{RT}{b₁}) are the parameters of Temkin isotherm.

Langmuir isotherm is characterized by the separation factor R_L expressed as follow:

\[ R_L = \frac{1}{1 + K_LC₀} \]

If R_L=0, the adsorption process is irreversible, normal if
0<R_L<1, linear if R_L=1 and unfavorable if R_L>1.

3. Results and Discussion

3.1. Characteristics of Activated Carbon

Figure 1A shown the FTIR spectrum of AC. The results revealed that the broad band observed at 3436 cm\(^{-1}\) may be attributed to the vibration of the O-H group. The peaks appeared at 1689 cm\(^{-1}\) and 1162 cm\(^{-1}\) were assigned to CO stretching vibration in carbonyl, lactonic and carboxyl functional groups [8]. The peaks at 2848 cm\(^{-1}\) and 2928 cm\(^{-1}\) were characteristics to the stretching vibration of C-H in aromatic rings from AC lignin content [15].

Figure 1B presented the scanning electron micrograph of AC with 1.46 kx magnification. The SEM image revealed that the AC surface is rough with numerous pores that could favor the adsorption of atrazine molecules.

3.2. Effect of Solution pH and Adsorption Mechanism

In this study, the initial pH of the atrazine solution was varied from 2 to 10 and the results obtained were shown in Figure 2A. Analysis of results indicated that the removal efficiency of atrazine decreased from 87.56% to 77% with increase in the pH from 2 to 10. Moreover, the zero-point charge (pH\(_{ZPC}\)) of AC was 3.2 [15]. Accordingly, at pH <3.2 the functional groups of AC surface were positively loaded and at pH>3.2 the surface of AC became negatively charged. Atrazine molecule is a weak base with pKa of 1.7, thus, at pH <1.7, the molecules of atrazine are protonated and the atrazine molecules get positively loaded. At pH>1.7, the surface of atrazine became negative loaded through excess of hydroxide ion from the solution. Therefore, the adsorption of atrazine may be due to hydrogen bonds established between the surface of activated carbon and the nitrogen atoms from atrazine molecules. Furthermore, atrazine structure shown π electrons, so, atrazine has a hydrophobic character. AC also owned a hydrophobic property due to its lignin content [14]. Thus, π-π interactions would be established between the atrazine molecules and the surface of the activated carbon. At pH value range 1.7-3.2, the attraction electrostatic interaction occurred between the positive loads from AC surface and the negative loads from atrazine molecule, which justified high adsorption value observed (Figure 2A). The decrease in adsorption of atrazine with pH>3.2 may be explained by the repulsion electrostatic interaction between the both negative charged particles. From results in Figure 2A, the high adsorption efficiency of atrazine was reached at pH = 2. But, in this work, the experiments were conducted at pH = 5 because the natural pH value of atrazine solution was around 5, which was in accordance with pH value reported by Kumar et al. [22]. Finally, the proposed mechanism for atrazine adsorption onto AC was presented in Figure 2B.
3.3. Effects of Contact Time and Kinetic Study

The effects of the contact time were carried out in the time range 0 -120 min with 50 mL of 50 mg/L of atrazine solution at pH 5, 7 and 9 and at room temperature. The results presented in Figure 3A shown that the removal percentage of atrazine increased with increase in the contact time from 0 to 120 min. The adsorption was fast at early of the process and became slow around 60 min in the contact time. Indeed, at the start of the reaction, there are a large number of available active sites on AC surface. As the contact time increased, the active sites from AC surface were gradually filled with the atrazine molecules, which led to a depletion in available sites for adsorption and resulted to equilibrium state noted in Figure 3A. The results also revealed that the equilibrium time was 60 min, however, in order to ensure that equilibrium was reached for all essays performed, a contact time of 120 min was chosen as equilibrium time, which was in accordance with those reported by Ghosh and Shirmardi et al. [23, 24]. In order to describe the adsorption mechanism, the kinetic models of pseudo-first-order, pseudo-second-order and intraparticle diffusion were studied. The plots of the kinetics models and the kinetic parameters were presented in Figure 3 (B, C, D) and Table 1. It is seen from the results in Table 1 that the pseudo-second order model well followed the experimental results with correlation coefficient $R^2$ greater than 0.99 for the three pH values tested. The experimental adsorption capacities were also in best agreement with those calculated. The plots of the intraparticle diffusion model (Figure 3D) presented two linear portions, indicating that the adsorption process happened in two stages. The first step was fast because the pores of the adsorbent were available at the start of the process, while the second step was slow and suggested the pores saturation. In addition, none of the linear portions passed through the abscissa origin, hence, the intraparticle diffusion model involved in the adsorption of atrazine.

![Figure 3. A- Effect of contact time, B - pseudo-second-order model, C - pseudo-first-order model, D - intraparticle diffusion model.](image)

| Table 1. Kinetic parameters. |
|--------------------------------|
| pH=5 | pH=7 | pH=9 |
| q_{e,exp} (mg/g) | 42.63 | 40.88 | 39.84 |
| q_{e,cal} (mg/g) | 24.24 | 24.63 | 22.26 |
| k_1 (min^{-1}) | 0.071 | 0.079 | 0.086 |
| R^2 | 0.94 | 0.97 | 0.903 |
| q_{w,exp} (mg/g) | 45.45 | 43.47 | 43.47 |
| k_2 (g/mg/min) | 0.0079 | 0.0074 | 0.0047 |
| R^2 | 0.999 | 0.998 | 0.997 |
3.4. Adsorption Isotherm Study

Langmuir, Freundlich and Temkin isotherms were studied to better understand the mechanism of atrazine adsorption. The obtained results and the isotherm parameters were shown in Figure 4 and Table 2. The results from Figure 4A revealed that the adsorption capacities of AC increased with increase in the atrazine concentration due to the growth in the driving force from the concentration gradient [25]. In addition, the results also denoted that the adsorption capacity decreased with increasing in the pH due to the electrostatic repulsion between the AC surface and the atrazine molecules. Moreover the results in the table 2 indicated that the adsorption of atrazine on AC may be described by Langmuir isotherm at pH 5, 7 and 9. The values of the separation factor \( R_L \) of Langmuir model were all less than 1, suggesting that the adsorption process of atrazine onto AC was normal and occurred with appearance of monolayers. The values of \( n \) constant from Freundlich isotherm were also included between 1 and 10, indicating a normal adsorption. The values of the \( b_T \) constant from the Temkin isotherm were low, which suggested that the adsorption process was less energetic. The low values of \( A_T \) (1.244, 1.875, 1.440 L/mg) suggested also the physisorption nature of the adsorption process. The values of the maximum capacities calculated according to the Langmuir isotherm were 66.66, 52.63 and 48.08 mg/g at pH 5, 7 and 9 respectively. Finally, the adsorption capacity at pH 5 was compared with those of various adsorbents reported in the literature (Table 3). The results pointed out a significant performance of prepared AC for atrazine removal compared to other adsorbents. Thereby, the peanut shell activated carbon can be used as efficient adsorbent for atrazine.

| pH=5   | pH=7   | pH=9   |
|--------|--------|--------|
| Langmuir |        |        |
| \( q_m \) (mg/g) | 66.66  | 52.63  | 48.08  |
| \( K_L \) (L/mg) | 0.134  | 0.162  | 0.141  |
| \( R^2 \) | 0.995  | 0.993  | 0.995  |
| \( n \) | 2.392  | 3.048  | 2.923  |
| Freundlich |        |        |
| \( K_f \) (mg/g (L/mg)^{1/n}) | 13.585 | 14.541 | 12.366 |
| \( R^2 \) | 0.970  | 0.898  | 0.923  |
| \( b_T \) (J.mol^-1) | 14.88  | 10.89  | 10.41  |
| Temkin   |        |        |
| \( A_T \) (L/mg) | 1.244  | 1.875  | 1.440  |
| \( R^2 \) | 0.990  | 0.944  | 0.950  |
4. Conclusion

The results of this study revealed that the peanut shell activated carbon shown high adsorption potential toward atrazine. The pseudo-second-order kinetic well described the adsorption process than the pseudo-first-order model. The equilibrium data at different pH were best fitted to Langmuir isotherm model. The maximum adsorption capacity 66.66 mg/g determined at pH 5 and at 30°C was significantly higher than of numerous adsorbents reported in literature. Therefore, the prepared activated carbon could be used as efficient adsorbent for atrazine and other pesticides removal from contaminated water.

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Table 3. Adsorption capacities of various activated carbons.

| Adsorbent                                           | qmax (mg/g) | pH | Contact time (h) | T(°C) | References       |
|----------------------------------------------------|-------------|----|-----------------|-------|-----------------|
| Desert Date Seed Shell Activated Carbon            | 3.235       | 7  | na              | 25    | 8               |
| Activated peanut husk                              | 4.12        | na | 3               | 25    | 14              |
| Granular carbon                                    | 5.0         | 5  | 24              | 25    | 22              |
| Activated carbon                                  | 13.95       | 6  | 2               | 25    | 24              |
| Peanut shell activated carbon                      | 66.66       | 5  | 2               | 30    | This study       |

na: not available
Adsorption of Atrazine from Aqueous Solution onto Peanut Shell Activated Carbon: Kinetics and Isotherms Studies

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