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Research Article

Study of the Adsorption of Difenoconazole on Char in Aqueous Medium

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Abstract

This study focuses on the use of a new plastic waste polythene terephthalate (PET) adsorbent in a physico-chemical process for liquid effluent treatment. First, the char was characterized by determining the iodine and methylene blue indices as well as the zero charge point. The experimental conditions were optimized by evaluating the influences of pH, adsorption kinetics, char mass and initial concentration of difenoconazole. The results of the characterization revealed that the zero charge point was less than 7 (6.66), the iodine and methylene blue indices were equal to 689 mg/g and 315 mg/g respectively. Adsorption studies showed a better elimination of difenoconazole under acidic conditions, with a rate of 55.29% at pH 2. Kinetics are rapid and equilibrium is reached after 60 minutes. Experimental results indicate that a mass of 0.01 g removes 53.26% of the pesticide and that the adsorption capacity increases with the concentration of the pesticide. The study of isotherms showed that the Freundlich model better describes the process of adsorption of difenoconazole on the PET char. The adsorption of difenoconazole on the char is therefore physical type. It is dominated by π-π, dipole-dipole and H bond interactions.

Keywords

Char, Adsorption, Pesticide, Difenoconazole, Plastic Waste

1. Introduction

Intensive and inappropriate use of pesticides in agriculture causes degradation alarming nature of the environment [1-3]. These synthetic chemicals transported by water rain (infiltration or runoff) present significant risks to ecosystems aquatic and human health due to their high toxicity even at low quantities [4]. In Indeed, the consequences of water pollution are very serious and can cause destruction of the aquatic environment, the life of aquatic flora and fauna and various human diseases [5]. Of more, because of the stability and low biodegradability of certain pesticides or their metabolites, biological treatments are difficult to apply, thus promoting the accumulation of these toxic products in the environment in a worrying manner. This is why it is very essential to develop simple and inexpensive techniques for the treatment of effluents liquids.

To treat liquid effluents, several techniques can be used, including coagulation, flocculation, chemical oxidation, membrane filtration, adsorption etc. [6]. However, adsorption has been the subject of particular attention from the entire scientific community for its ease of implementation and low

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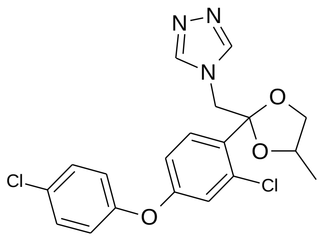
cost. Several studies have therefore looked into this phenomenon more suitable for wastewater treatment [6-8]. This is how, in the present study, we are interested in the elimination of the pesticide difenoconazole by adsorption on the char produced from waste polyethylene terephthalate plastic bottles.

2. Materials and Methods

2.1. Pesticide

Table 1. *Characteristics of DFZ.*

Compound	Nature	Family	Chemical formula	Molar mass (g/mol)	Structural Formular
Difenoconazole	Fungicide	Triazole	$C_{19}H_{17}Cl_2N_3O_3$	406,26	

The pesticide used in this study is difenoconazole (DFZ). It is a fungicide from the family of triazoles. It belongs to the group of endocrine disruptors, known to harm human health and cause acute and chronic toxicity in aquatic environments [9]. The DFZ constitutes a serious threat to aquatic biota and, once degraded, the resulting compounds remain toxic to the environment [9]. It is frequently detected in aquatic environments [10]. Some characteristics of this pesticide are mentioned in Table 1.

2.2. Adsorbent Material

The adsorbent used in this work is char synthesized from plastic bottles in polyethylene terephthalate by Boukongou [6]. It was characterized by determining the blue index of methylene and iodine index to evaluate respectively the mesopores and micropores of the adsorbent [7, 11]. The point of zero charge, defined as the pH for which the overall charge of the surface area of the adsorbent is zero was also determined to predict the types of interactions adsorbent-adsorbate.

2.3. Adsorption of Difenoconazole

The adsorption tests were studied in stirred reactors protected from light and at temperature ambient. We studied the effect of the pH of the reaction medium, the contact time, the mass of the adsorbent and the initial concentration of the adsorbate.

2.3.1. Influence of pH

Adsorption was carried out as a function of pH in the range of 2 to 12, to determine the pH optimal reaction medium favoring good elimination of the pollutant. Indeed, the pH is a very important parameter in any adsorption study because it can modify both the behavior of the adsorbent and the adsorbate. Thus, 0.01 g of tank powder was brought into contact with 20 mL of a DFZ solution with a concentration of 60 mg/L.

2.3.2. Adsorption Kinetics

In order to know the adsorption kinetics, that is to say the time necessary to reach adsorption equilibrium, we brought 0.01 g of char into contact with 20 mL of a solution of DFZ with an initial concentration of 60 mg/L. The adsorption kinetics was monitored over an interval of time from 10 to 90 minutes with a gradient of 10 minutes.

2.3.3. Influence of the Mass of the Adsorbent

Knowing the mass of the adsorbent capable of eliminating a large quantity of pollutant is necessary to optimize adsorption. The study was carried out by stirring 20 mL of pesticide at 60 mg/L, with different masses of char (0.01-0.09 g) in 250 mL reactors, for 60 minutes.

2.3.4. Influence of the Initial Concentration of the Adsorbate

To know up to what concentration of pesticide the tank is capable of eliminating, we have mixed 20 mL of pesticide solution at concentrations of 10 to 70 mg/L with masses of 0.01 g of char in 250 mL reactors at pH 2. The mixtures were stirred for 60 minutes.

2.4. Modeling of Adsorption Isotherms

Langmuir and Freundlich isotherms were used to model the results experimental. The characteristic parameters for each isotherm were determined [7, 8, 13, 14].

3. Results and Discussion

3.1. Characterization of the Char

3.1.1. Char Porosity

The porosity of the char used was evaluated by determining its iodine indices (microporosity) and methylene blue (mesopority). The results of this study are presented in Table 2. The iodine index obtained is equal to 689.10 mg/g, a result close to that of Andzi et al. [7]. According to these authors, the microporosity of an adsorbent is quite important if the quantity of iodine adsorbed is between 900 and 1200 mg/g. It is therefore possible that the majority of pores in the char used are mesopores. This hypothesis is confirmed by the methylene blue index, because the quantity of methylene blue adsorbed is 314 mg/g. Therefore, the amount of iodine adsorbed by the char indicates that there are micropores in this material, but these are in the minority by relation to mesopores; this could therefore promote good adsorption of molecules large, like the DFZ.

Table 2. *Iodine and blue d indices. [15].*

Adsorbent	Iodine indice (mg/g)	Methylene blue indice (mg/g)
Char	689,10	314,95

3.1.2. Point of Zero Charge (pHpcn)

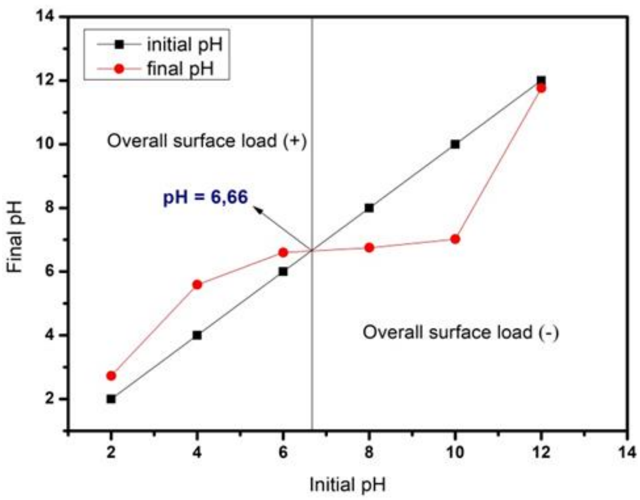


Figure 1. *Point of zero charge.*

The adsorption of the adsorbate on the surface of the adsorbent strongly depends on the pH of the solution to be treat as well as the point of zero charge. The zero charge point of our adsorbent is equal to 6.66. Thus, in solutions where the pH is greater than 6.66, the surface of the adsorbent develops a negative charge, therefore the adsorption of positively charged substances is favored. On the other hand, if pH < pHpcn, the overall surface of the adsorbent carries a positive charge, which creates repulsive interactions with positively charged substances [16].

3.2. Adsorption Study

3.2.1. Influence of pH

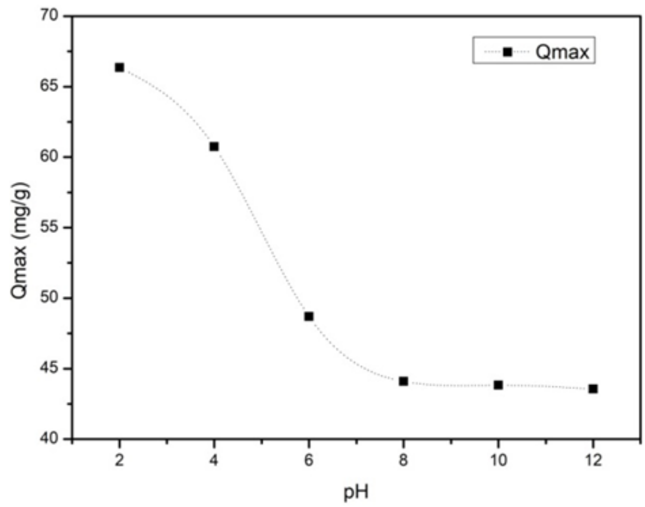


Figure 2. *Influence of reaction medium pH on DFZ adsorption.*

The quantities of pesticide retained by the char as a function of pH are shown in Figure 2. In this study, adsorption capacities were 66.35 mg/g at pH 2, 60.75 mg/g at pH 4, 48.70 mg/g at pH 6, 44.09 mg/g at pH 8, 43.82 mg/g at pH 10 and 43.55 mg/g at pH 10. The adsorption of the pesticide is high at pH 2, with an elimination rate of 55.29%, and the amount adsorbed decreases as the pH of the solution increases. The results obtained at zero load point (Figure 1) indicate that the adsorbent surface is positively charged at pH 2. The results of this study are consistent with previous observations which showed that acid conditions were favourable for the removal of difenoconazole from the surface of a adsorbent loaded positively [12]. Sukran A. et al. reported that under basic conditions, the decrease in adsorbed amount could be explained by competition between hydroxyl ions (-OH) and methyl ions (-CH3) of DFZ to interact with the cationic structure of the adsorbent [12]. The positive behaviour of char in acidic conditions could be dominated by the filling of microporosity, π-π, dipole-dipole interactions and H bond. Evaluating the effect of pH on the adsorption of difenoconazole by Chitosan, Sukran A. et al. showed adsorption capacities of 9 µg/mg at pH 3, 11 µg/mg at pH 4, 12.7 µg/mg at pH 5, 11 µg/mg at pH 6, 8 µg/mg at pH 7, and 7 µg/mg at pH 8. The high adsorption capacity was obtained under acidic conditions at pH 5. The results reported here show that PET char is effective for the removal of organic pollutants.

3.2.2. Adsorption Kinetics

Figure 3 presents the adsorption capacities of DFZ as a function of contact time. We observe a first rapid adsorption phase lasting 10 and 20 minutes, followed by an adsorption phase slow between 20 and 50 minutes before reaching adsorption equilibrium at 60 minutes with a rate elimination of 85.24%. The high speed of adsorption observed in the first 20 minutes for the DFZ could be explained by the initial abundance of free active sites on the surface of the adsorbent. The second phase of slow adsorption reflects the progressive saturation of the active sites until equilibrium is reached, marking the total saturation of active sites. These results corroborate much of the previous work [13, 17-19]. This is encouraging to compare with the results of Bayan K. et al., who found that difenoconazole adsorption on Cell-X and Cell-D polymers was rapid and stabilized at about 22 minutes [20]. The removal of difenoconazole from celluloses was explained by the ability of adsorbents to absorb the pesticide through intermolecular forces, including H-bond, π-π-interaction and dipole-dipole bond.

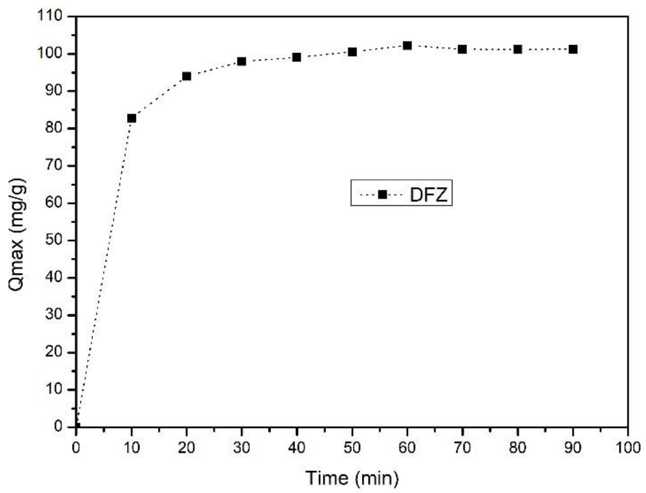


Figure 3. *Influence of contact time on DFZ adsorption.*

3.2.3. Influence of Adsorbent Mass

The results of DFZ adsorption as a function of polyethylene terephthalate char mass are presented in Figure 4. The increase in the mass of the adsorbent in the reactor generates a significant number of active sites in solution, which would promote increasing adsorption of DFZ. However, we observe from Figure 4 that the adsorbed quantity decreases when the mass of the adsorbent increases. This behavior could be linked to the phenomenon of steric hindrance. Indeed, larger quantities of the adsorbent lead to the formation of agglomerates of the particles preventing the adsorbates from accessing the active sites on the surface of the adsorbent. Which reduces drastically reduces the adsorption capacity of the adsorbent. These results are consistent with those obtained by Andzi et al. [7]. These authors showed that increasing the mass of the adsorbent led to a gradual reduction in the quantity of pollutant adsorbed. Similar results have also been reported by several authors [21, 22]. An elimination rate of 53.26% is obtained for a mass of 0.01 g.

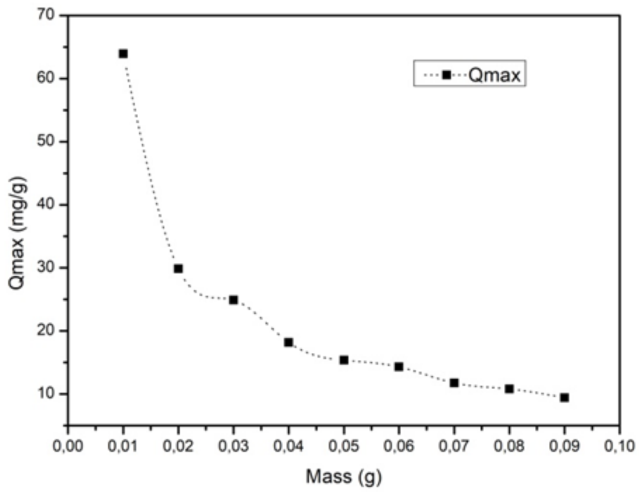


Figure 4. *Influence of adsorbent mass on DFZ removal.*

3.2.4. Influence of the Initial Adsorbate Concentration

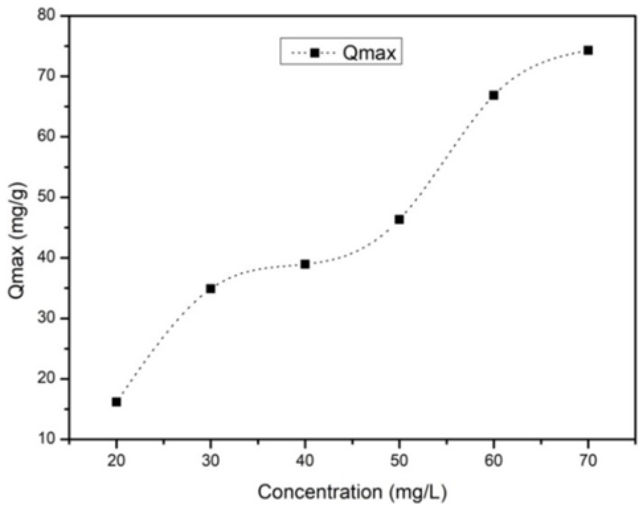


Figure 5. *Influence of initial DFZ concentration.*

The results illustrated in Figure 5 show that the adsorption capacity increases with increasing the initial concentration of the pesticide. This behavior could be explained by the diffusion of pesticide molecules from the solution to the surface of the adsorbent, accelerated by the increase in pesticide concentration. Indeed, the increase in concentration promotes the increase in the driving force of the concentration gradient [19]. This result was also reported by Bennani Karim et al. [8].

3.3. Modeling of Adsorption Isotherms: Langmuir and Freundlich Models

The linear equation of Langmuir was applied to the experimental results and the adsorption parameters are reported in Table 3. We note that the coefficient of r^2 correlation (r^2 = 0.71) is very low for the char. This poor correlation between the data experimental and the Langmuir model indicates that the nature of the char surface is not homogeneous [8, 23]. Therefore, the Langmuir isotherm cannot be used to describe adsorption of difenoconazole by char.

Table 3. *Langmuir parameters.*

K_L (L/mg)	Qmax (mg/g)	r^2
0,009	168,06	0,61

The adsorption parmeters reported in Table 4 were obtained by applying the linear equation of the Freundlich model. We notes that the correlation coefficient r^2 (r^2 = 0.91) is very close to unity for our adsorbent. This good correlation between the experimental data and the Freundlich model indicates the heterogeneous nature of the char surface with pesticide-pesticide interactions [8, 23]. The value of 1/n gives an indication of the validity of the adsorption of the char-pesticide system. The numerical value of 1/n obtained from the slope of the line lnqe=f(lnCe) is equal to 0.334 for the char. This value is between 0 and 1, which indicates that the adsorption is favorable [23].

The Freundlich model has a better correlation coefficient r^2 than that of Langmuir; this indicates that the Freundlich isotherm describes adsorption better than that of Langmuir. By Therefore, the adsorption of difenoconazole on char is of physical type.

Table 4. *Freundlich parameters.*

K_F (L/mg)	1/n	r^2
1,39	0,33	0,91

4. Conclusion

Experimental results of the adsorption of chlorpyrifos-ethyl on polyethylene char terephthalate (PET) have shown that its retention is rapid. The mass of the adsorbent plays a very important role important. Indeed, the smaller the mass, the better the adsorbent adsorbs the pesticide. In the middle basic, the retention of the pesticide is better. The Freundlich isotherm model better describes the phenomenon of adsorption of difenoconazole on the PET char. Thus, the PET char is a adsorbent which has interesting adsorption capacities which could therefore be an alternative to other more expensive adsorbent materials such as activated carbon. Additional work is needed, including the structural characterization of PET chars to optimize their adsorption capacity.

Abbreviations

PET	Polyethylene Terephtalate
DFZ	Difenoconazole

Conflicts of Interest

The authors declare no conflicts of interest.

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