



REMOVAL OF CHEMICAL OXYGEN DEMAND FROM PHARMACEUTICAL WASTEWATER BY ADSORPTION ON ANTHRACITE. ADSORPTION ISOTHERMS AND THERMODYNAMICS

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The characterization of the pharmaceutical wastewater by physicochemical analysis of some parameters showed a significant pollution load, expressed particularly by organic pollutants (chemical oxygen demand and biological oxygen demand). The removal of chemical oxygen demand by adsorption on anthracite is investigated in this study. The adsorption isotherms are realized in batch system; several working parameters, such as mass of adsorbent, contact time, temperature and particle size of anthracite were studied in an attempt to achieve a higher removal efficiency.

The adsorption treatment achieved a maximum reduction of 70% for chemical oxygen demand under the following experimental conditions: 20°C, 3 g of adsorbent, contact time: 1 hour and particle size of 0.6 mm. The adsorption follows well the Freundlich model and the adsorption kinetics is the pseudo-first-order type. The free energy change of COD adsorption on anthracite was calculated, and it indicates that adsorption is a spontaneous and physical process.



INTRODUCTION

Pharmaceutical compounds are being used for several beneficial purposes in modern society. Many pharmaceutical industries are responsible to generate toxic effluent as a consequence of their operation. The wastewater generated from these industries has a composition of complex and it contained many kinds of organic pollutants in high concentrations, NH-N and high levels of suspended solids, color depth, toxicity and other features.^{1,2}

The main pollutant releasing from this industrial wastewater is oxygen function, and is measured in chemical oxygen demand (COD) and biological oxygen demand (BOD). It is estimated that approximately half of the pharmaceutical wastewaters produced worldwide are discarded without specific treatment.^{3,4} The effect of pharmaceutical

wastes in the environment is a raising concern about the potential environmental consequences and it has an impact on the surface water, aquatic species, human health and surrounding lands, which may cause a serious problem to drinking water directly or indirectly. The effect of these contaminants depends upon the processing technology, nature of chemicals used, the complexity and characteristics of wastewater discharged.⁵

Treatment of these wastes is therefore of paramount importance. Various techniques employed in the treatment of pharmaceutical wastewater are essentially biological and physicochemical processes such as aerobic and anaerobic biological process, coagulation, flocculation, sedimentation. These techniques have shown limited success for the treatment of pharmaceutical wastewater due to the nature and composition of pharmaceutical effluents.

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For example, because of the elevated COD content of pharmaceutical wastewater, anaerobic treatment would come to mind but is not always feasible in particular because of the high total dissolved solids (TDS) content of such wastewater which interferes with the activity of methanogenic bacteria.⁶

Adsorption on activated carbon has been a useful and effective process for the purification of industrial and hazardous wastewaters, as well as for the removal of organic pollutants from water.⁷

However, due to high cost of activated carbon, generally used as an adsorbent, the possibility of using inexpensive materials as alternatives was explored by many researchers in the past years.⁸ The development of low-cost adsorbents has led to the rapid growth of research interests in this field. A detailed review of the literature observed that anthracite, as natural, inactivated adsorbent, is the energy source of high level carbonation, whose ability to adsorb known since ancient times.⁹ Anthracite is a type of coal, with the highest carbon count, between 29 and 98%, and contains the fewest impurities of all coals.¹⁰

The aim of the project is to examine the potential of anthracite as an adsorbent material for the removal of chemical oxygen demand from pharmaceutical wastewater by studying the influence of several experimental parameters such contact times, mass of adsorbent, temperature and particle size of anthracite.

EXPERIMENTAL

Physicochemical characterization of pharmaceutical wastewater

The pharmaceutical wastewater studied is stored at 4°C before its use to avoid changes in the physico-chemical properties.

All parameters may be altered, and are analyzed in the laboratory in the shortest possible time in accordance with conservation rules and standardized analysis methods.

The pH, the turbidity and the conductivity of the solution are measured by using, respectively, a pH meter (HANNA HI 9812-5), a turbidimeter (HANNA HI 88713-ISO) and a conductivity-meter (ISO Method HACH 7027). The analysis of chlorides is carried out by Mohr method,¹¹ the COD and BOD are achieved via the ISO 6060-1989 standard experimental protocol for the first parameter and the French standard experimental¹¹ for the second.

Adsorption tests of COD from pharmaceutical wastewater

Anthracite was crushed, ground and dried at 120°C in an oven for 2 hours before being used. After drying, the adsorbent is stored in sealed glass containers. The adsorption isotherms are investigated in batch sorption equilibrium experiments.

The determination of removal efficiency of COD on used anthracite necessitates previous optimization of two key parameters: the contact time and the mass of the adsorbent.

Various masses of anthracite (0.5, 1, 1.5, 2 and 3 g) are mixed with 100 mL of pharmaceutical wastewater solution in a series of erlenmeyer flasks. After stirring at variables contact times, maintained at a constant temperature in a water bath (Memmert), the samples are filtered then the residual concentration of COD is measured via the experimental protocols of ISO 6060-1989 standard. The calculation of COD removal rate, expressed as a percentage, is based on the following formula:

$$COD\% = \frac{C_i - C_f}{C_i} 100 \quad (1)$$

C_i : initial concentration of COD (mg/L)

C_f : final concentration of COD (mg/L)

The effect of the particle size (3 g of anthracite at different particle size: 0.6, 0.8, 1.0, 1.2, 1.4 and 1.6 mm and contact time of 1 hour), of the temperature (20, 30, 40 and 50 °C with 3 g of anthracite) and the initial concentration of COD (1 hour of contact time, 3 g of anthracite and different concentrations of COD obtained by diluting wastewater) has been studied.

The adsorption capacity of anthracite is calculated using the expression:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

Q_e : the adsorption capacity, at equilibrium, of COD per unit mass of the adsorbent (mg/g),

C_0 : the initial COD concentration (mg/L),

C_e : the concentration at equilibrium (mg/L),

m : the mass of adsorbent (g),

V : the solution volume (L).

In order to investigate the adsorption mechanism, the Langmuir¹² and Freundlich¹³ models were used to fit COD adsorption isotherm data onto anthracite. The linearized Langmuir adsorption isotherm equation, which is valid for monolayer sorption onto a surface with finite number of identical sites, and Freundlich adsorption isotherm equation, which adopts multilayer adsorption on heterogeneous surfaces are, as follow:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m C_e} \quad (3)$$

$$\ln Q_e = \ln Kf + \frac{1}{n} \ln C_e \quad (4)$$

Q_e : adsorption capacity, at equilibrium, of solute per gramme of adsorbent (mg/g),

C_e : the equilibrium concentration of adsorbate in solution (mg/L),

Q_m : maximum adsorption capacity of Langmuir (mg/g),

b : Langmuir constant (L/mg),

Kf and n : empirical constants of Freundlich (the capacity and the intensity of adsorption).

RESULTS AND DISCUSSION

Characteristics of the pharmaceutical wastewater

The physicochemical analysis of the pharmaceutical wastewater studied is listed in Table 1. It

shows a comparison between the obtained values of this wastewater with the Algerian national standards defining the limit values of industrial effluent liquids discharges.¹⁴ From this table, it is clear that some values, such as turbidity (5000 NTU), BOD (4100 mg/L) and COD (1380 mg/L) have exceeded the Algerian standards.

In view of these results, it is worth to note that this pharmaceutical wastewater has organic pollutants. Thereby, the biodegradation of these matters causes oxygen consumption where a possible eutrophication of the receiving environment with a deterioration of the fauna and flora and the creation of harmful resistant species can take place. All these observations are a proof this wastewater has to be treated.

Chemical characterization of anthracite

Anthracite was used without any chemical pretreatment. It was chemically stable and insoluble

in water. The physicochemical characteristics of anthracite are presented in Table 2.

Adsorption results of COD on anthracite

Influence of the mass of the adsorbent and adsorption kinetics

In general, the search for the adsorption kinetics, depending on the mass of the adsorbent, is a prerequisite for the determination of the contact time or equilibrium between the solute and the adsorbent, in view optimization of adsorption.^{16,17} According to the results reported in Fig. 1, it is noted that the performance of the removal of COD increases with the mass of anthracite. For masses of adsorbent of 0.5, 1, 1.5, 2 and 3 g, result in adsorption efficiencies of 27, 30, 38, 60 and 70 % respectively. With the increase in adsorbent amount, adsorption sites become abundant compared to oxygen demand present in the solution. Therefore adsorbent dose of 3 g was used for all further experiments.

Table 1

Physicochemical characterization of the pharmaceutical wastewater

Parameters analyzed	Values	Algerian standards
Temperature (°C)	80	30
pH	9.2	6.5-8.5
Conductivity (mS/cm)	3.43	/
Turbidity (NTU)	5000	/
COD (mg/L)	1380	130
BOD (mg/L)	4100	40
Suspended matter (mg/L)	7450	40
Chlorides (mg/L)	280.82	/

Table 2

Physicochemical characteristics of anthracite¹⁵

Parameters	Values
Carbon (%)	90
Volatile materials (%)	6.7
Sulfur (%)	0.8
Ash (%)	3-5
Moisture (%)	1.5
Particle size (mm)	0.6-1.6
Density (g/cm ³)	1.4

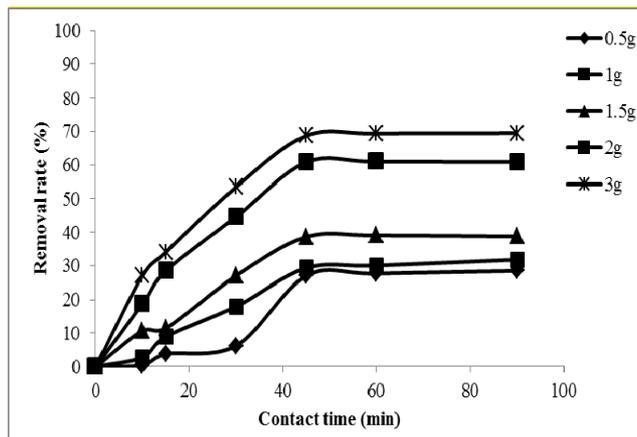


Fig. 1 – Influence of the adsorbent mass on adsorption rate of COD as function of contact time.

For kinetics adsorption of COD by anthracite, Fig. 1 shows that the pseudo equilibrium is reached after 45 minutes of contact time for all adsorbent masses. The shape of the kinetic curve possesses two parts, the first shows the exponential adsorption after 45 minutes, while the second part is stationary platen with slower adsorption to saturation of adsorbent.

The same removal rate was found by Saleem¹⁸ using the adsorption of COD onto activated carbon after a stirring time of 5 hours (70%). Shao *et al.*¹⁹ have found a removal efficiency of COD, in pretreatment process of pharmaceutical wastewater onto thiamine-modified bentonite, of 47.98 % using 4g/L of adsorbent.

Determination of kinetic model

In the order to investigate the mechanism of adsorption kinetics of COD onto anthracite, the kinetics models pseudo-first order²⁰ and pseudo-second order²¹ were applied to the experimental data.

The linearized form of the pseudo-first order can be expressed as follows:

$$\ln(q_e - q_t) = K_{Lag}t + \ln q_e \tag{5}$$

where q_t and q_e are the amount adsorbed at time t (mg/g) and at equilibrium (mg/g) respectively, K_{Lag} is the rate constant (min^{-1}) of the pseudo-first order adsorption process.

The pseudo-second order kinetic model can be written as follows:

$$\frac{t}{q_t} = \frac{1}{q_e^2 K_b} + \frac{t}{q_e} \tag{6}$$

K_b : is the pseudo-second order rate constant (g/mg min).

According to Fig. 2 and 3, the plot of $\ln(q_e - q)$ versus t for pseudo-first order model yields very good straight lines (correlation coefficient $R^2 > 0.99$) as compared to the plot of pseudo-second-order ($R^2 = 0.95$).

Hence, the pseudo-first order kinetic model seems to be best fitted for the experiment with rate constant K_{Lag} equals 0.051min^{-1} .

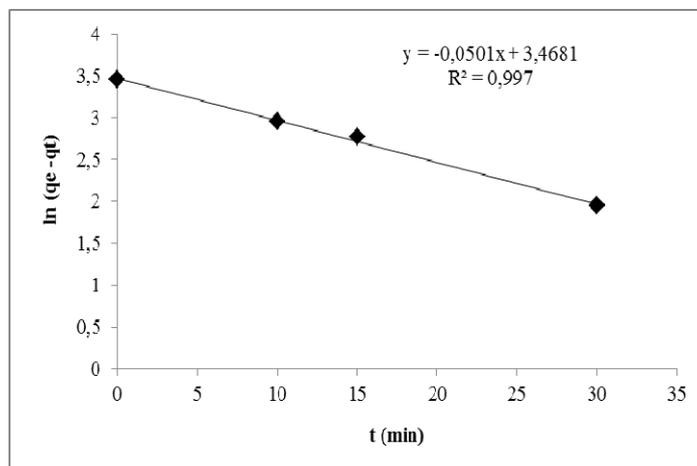


Fig. 2 – Linearisation as pseudo first order model.

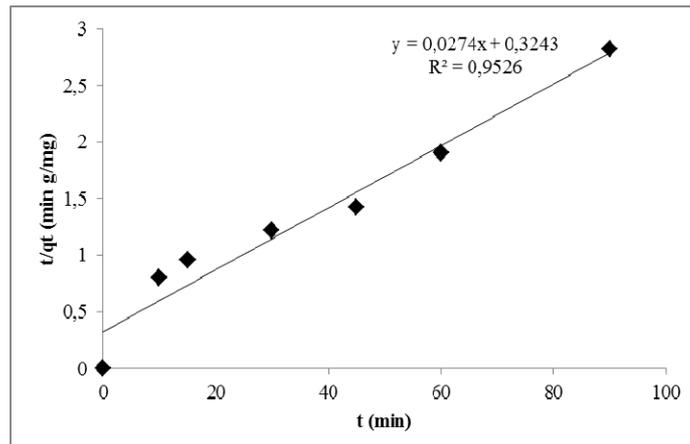


Fig. 3 – Linearisation as pseudo second order model.

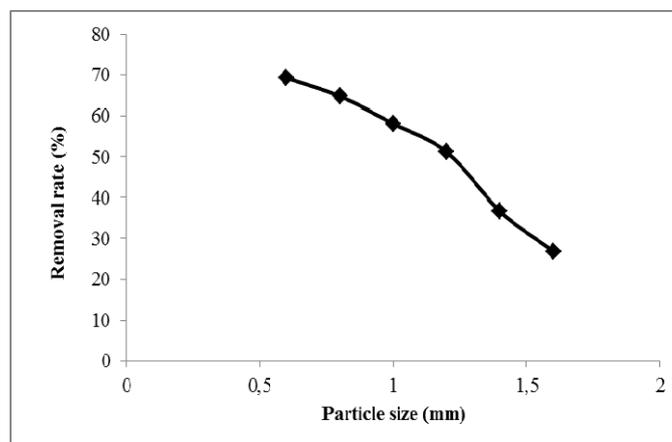


Fig. 4. Influence of *particle size* on the removal rate of COD.

Influence of particle size

Particle size significantly influenced the treatment performance of the anthracite. The plot of percentage removal of COD against particle size is depicted in Fig. 4. It shows that removal efficiency of adsorbent for COD decreases with increasing particle size. Highest removal was observed for particle size of 0.6 mm of anthracite.

This is probably due to the fact that, with the decrease of particle size, the surface areas of the adsorbents are increased, which provide greater number of adsorption sites for COD to adsorb onto adsorbent.¹⁰

Effect of temperature

Measurements of the performance of COD removing at different temperatures (20, 30, 40 and 50°C) yields the results illustrated in Fig. 5. At 20°C, the reduction rate of the COD is about 70 %. The increase in sample temperature at 30, 40 and 50°C reduces the effectiveness of treatment. At 50°C, the removal rate was reduced by about 30% compared with the test at 20°C. Thus, the increase

in temperature considerably reduces the stability of bonds between the active sites of anthracite and organic compounds.

Modeling of the adsorption equilibrium

Adsorption isotherms were employed to characterize the adsorption of adsorbate onto adsorbent from pharmaceutical wastewater. Adsorption isotherms can provide information about the nature of the physico-chemical interaction involved in the adsorption process.²²

The experiment was carried out at different initial COD concentrations, obtained by dilution of pharmaceutical wastewater, for an adsorbent dose of 3g and contact time of 1 hour. As shown in Fig. 6, the results indicated that as the initial COD concentration increased, the adsorption capacity of the COD also increased. The observation is apparent due to the availability of higher number of COD resulting in higher concentration gradient. With the increase in COD concentration in solution phase, the availability of COD also increases at the solid–solution interface, resulting in the increase in adsorption performance.

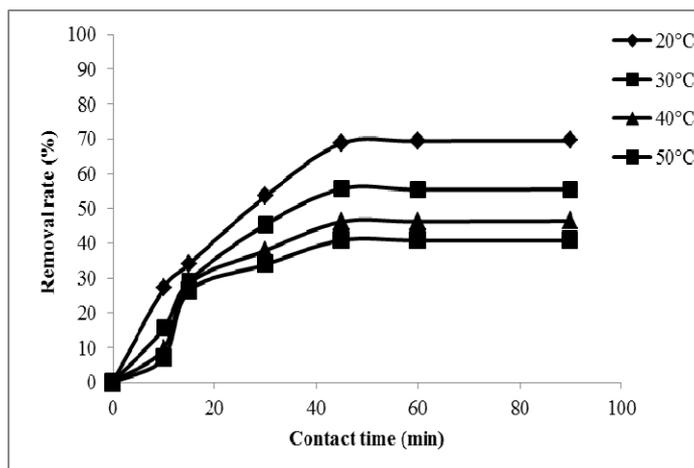


Fig. 5 – Influence of temperature on removal of COD.

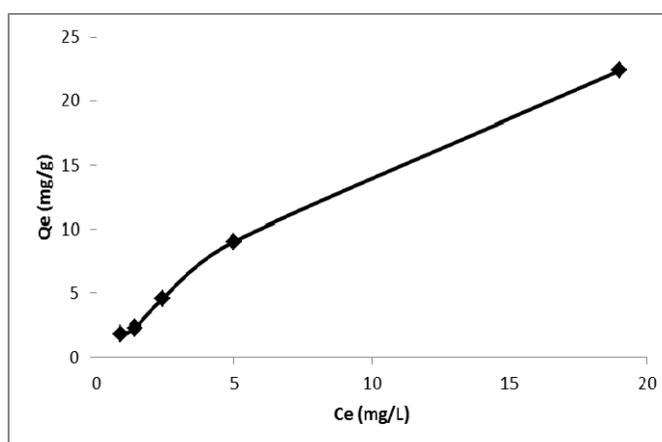


Fig. 6 – Adsorption isotherms of COD.

Table 3

Values of characteristics constant of the two adsorption models

Langmuir Model			Freundlich Model		
Qm (mg/g)	b (L/mg)	R ²	Kf	n	R ²
36.5	0.056	0.9667	2.0	1.17	0.9858

Referring to the classification of Giles *et al.*,²³ this corresponds to the isotherm type L. In this type of adsorption isotherm, the initial part informs about the availability of active sites for the adsorbate and the bearing means forming a monolayer. The curve indicates that a large amount of COD adsorbed at low concentrations when active sites are available. When the concentration increases, it becomes increasingly difficult for the adsorbate to find vacant sites to set which promotes forming a monolayer.

The obtained isotherms, described by the two linear models Langmuir and Freundlich (Fig. 7 and 8), show that the linear coefficient of determination of the Freundlich model is closer to 1 (0.9858), so the adsorption equilibrium is described better by

this model. This may be explained by the continuous distribution of adsorption sites and also by the presence of unsaturated sites.

The different characteristic constants of Langmuir and Freundlich isotherms are grouped in Table 3.

Adsorption thermodynamics

The transformation of adsorbate from solution to the surface of adsorbent affects the thermodynamic properties of the system.²⁴ The free energy change of the adsorption process, ΔG° , can be calculated by equation 7:

$$\Delta G^\circ = -RT \ln K_0 \quad (7)$$

where: R (8.314 J/K mol) is ideal gas constant, T (K) is absolute temperature and K_0 is partition coefficient.

$\ln K_0$ can be obtained from the intercept of the straight line plots of $\ln (Q_{eq}/C_e)$ versus Q_{eq} .²⁵ This method^{26, 27} was used to calculate the ΔG° value in this research.

According to experimental data, the relationship graph of $\ln (Q_{eq}/C_e)$ versus Q was obtained in Fig.9. The process of COD adsorption on anthracite is spontaneous and physical because the ΔG° value was below zero (-1.912 kJ/mol), and its absolute value is in the range of 0~20 kJ/mol.²⁸

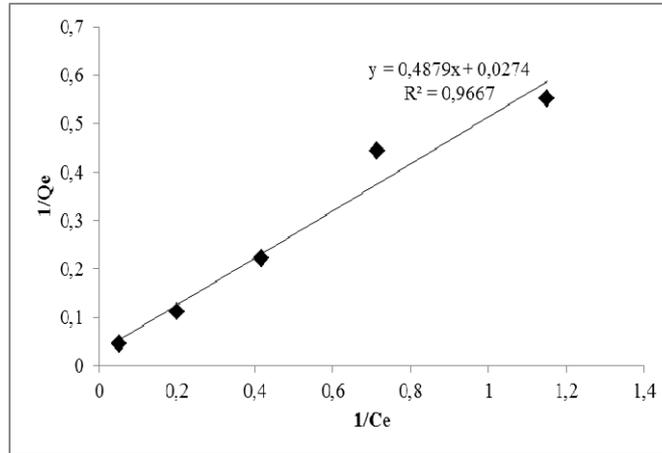


Fig. 7. Isotherm adsorption modeling of COD on anthracite according to Langmuir isotherm.

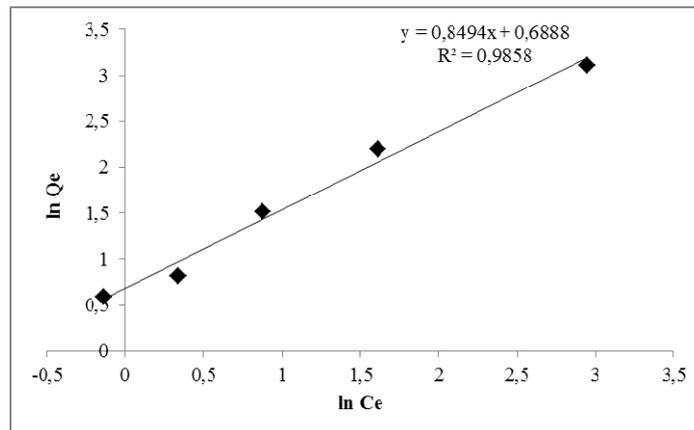


Fig. 8. Isotherm adsorption modeling of COD on anthracite according to Freundlich isotherm.

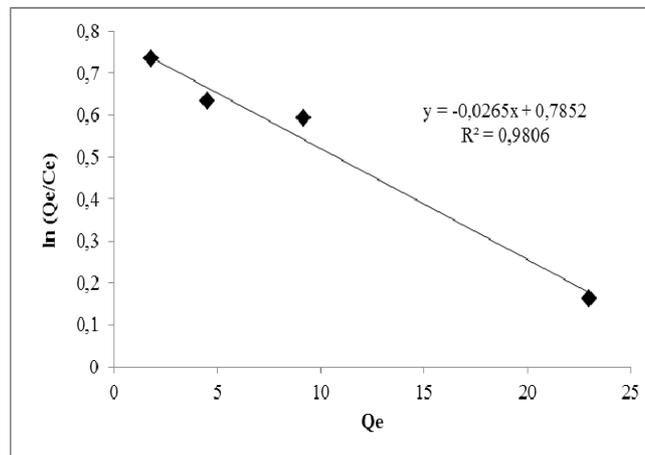


Fig. 9. Plot of $\ln (Q_{eq}/C_{eq})$ versus Q for COD adsorption on anthracite.

CONCLUSIONS

The physicochemical analysis of the studied pharmaceutical wastewater indicates that Algerian standards defining the limit values of industrial effluents liquids discharges are often exceeded for many parameters (COD, BOD, turbidity and suspended matter). Treatment of these waters is imposed.

The objective of this work is to remove the COD from this effluent by the adsorption process on natural adsorbent "anthracite".

The results of adsorption treatment show that the equilibrium time is reached in less than 1 hour. The best removal efficiency is estimated at 70% in specific experimental conditions (mass of adsorbent equals 3 g, particle size of anthracite 0.6mm and ambient temperature 20°C). The adsorption follows well the Freundlich model and the adsorption kinetics is rapid and it is of the pseudo-first-order type.

According to the result of the thermodynamic, the negative value of change in Gibbs free energy (ΔG°) indicates that adsorption of COD on anthracite is spontaneous.

Finally, we can say that the treatment process selected in this work, gives a very acceptable removal efficiency of COD. The improved results obtained by the use of other conditions, is possible to get the most of this natural adsorbent.

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