Organic pollutants removal from petroleum refinery effluents through adsorption using anthracite coal: Kinetics, Isotherms, and Thermodynamic Modeling

M. Ziati[1,2], S. Khemili[1], and A. Metali[1]

[1] Laboratory of Soft Technologies, Physicochemical, Valorization of Biological Materials and Biodiversity, Chemistry Department, Faculty of Sciences, M'hamed Bougara University, Boumerdes 35000 (Algeria).
[2] Laboratory of Applied Chemistry and Materials, Chemistry Department, Faculty of Sciences, M'hamed Bougara University, Boumerdes 35000 (Algeria).
corresponding author: `m.ziati@univ-boumerdes.dz` ; Tel: Tel : +21324952397, 213662957698
`khemilisara35@gmail.com`
`a.metali@univ-boumerdes.dz`

Abstract.
The wastewater from petroleum industries mainly contains oil, organic matter and other compounds. Their physicochemical characterization showed a considerable organic pollutant load which exceeds the Algerian guidelines establishing the limitations for industrial liquid effluent emissions, expressed in particular as chemical and biological oxygen demand and hydrocarbons (COD:268.5mg/L, BOD_5:183mg/L, and hydrocarbons:188mg/L). Their removal is an important challenge for remediation of large volumes of petrochemical effluents. The objective of this work is the elimination of COD and hydrocarbons from refinery effluent by the discontinuous adsorption on anthracite, a low cost and naturally abundant coal, as a potential adsorbent. Adsorption equilibrium and kinetics data were calculated and fitted to a variety of adsorption isotherms and kinetics models. The Langmuir isotherm corresponds very well to the equilibrium data of the two pollutants on anthracite with a correlation coefficient equal to 0.98. At 25^0C, the anthracite-organics adsorption system reached equilibrium in 120 minutes, and the adsorption kinetics followed the pseudo-second-order pattern with a rate constant value of 0.072 and 0.084g/mg.min for COD and hydrocarbons respectively. The pollutant removal percentage is 82% for COD and 94% for hydrocarbons at optimum mass of adsorbent=3g. The adsorption is spontaneous, according to thermodynamic studies, which suggest an endothermic process.

Keywords: Anthracite coal, chemical Oxygen demand, hydrocarbons, petroleum refinery wastewater, bath adsorption, adsorbent

1 Introduction

Large volumes of water are required in the refining of petroleum to generate valuable products including liquefied petroleum gas, jet fuel, gasoline, asphalt, diesel, and petrochemical feedstock through desalting, distillation, thermal cracking, catalytic, and treatment processes [1-4].

For this purpose, petroleum refineries produce large amounts of effluent, including oil well-generated water, which is typically refractory, and large quantity of organic and inorganic matter such as phenols, and hydrocarbons, minerals, gases, metal ions and anions of inorganic acids among others [5–8].

The volume of petroleum refinery effluents produced can differ somewhere in the range of 3-70 times the treated crude oil, approximately 468 gallons of water are required to refine a barrel of raw petroleum [8].

The wastewater is characterized by high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of around 150–250 mg/L and 300–600 mg/L respectively [9, 10–12], total suspended solids (TSS), ammonia, sulphides, total organic carbon, total petroleum hydrocarbon (TPH) and other toxic compounds, based on the operations and products from the producing industries [13-17], which is very hazardous and can linger in the environment for a long period. Direct discharge of these effluents could result in significant environmental contamination problems [18]. For living beings, the minimum amount of dissolved oxygen in a water environment is 2 mg/L [17]. The release of petroleum refinery effluents into water bodies, on the other hand, results in an excess of oxygen consumption due to bacterial oxidase of organic molecules [19]. If wastewater with high organic matter content flows into a river, the oxygen consumed for the oxidation of organic matter by the bacteria present in the river is faster than it dissolves in air. This resulted in the death of the fish, a consequence known as fish kill. As a result, creating an effective method for treating petroleum refinery effluent is critical for environmental reasons [20].

Very little research that has investigated the treatment of wastewater from the oil refinery sector, and its broader environmental implications from their discharged wastewater contaminants. The work carried out focused on membrane bioreactors [21], adsorption [22], biodegradation, ion exchange and flotation, electrochemical separation, biological activated carbon (AC), advanced oxidation techniques [23], and activated sludge system [24]. Nevertheless, there are obvious limits to these techniques due to the high cost of membrane and fouling problems, chemical agents, and activated carbon, etc. [25-28].

Adsorption using solid adsorbents is one of the most efficient methods for removal of organic contaminants during wastewater treatment. Its main advantages are simplicity of design and cheap start up and running costs[29].

For oily wastewater treatment, a variety of adsorption materials have been investigated, including activated carbon, coal, fiberglass, peat, sand, bentonite, attapulgite, amberlite, polypropylene, and organo clay [30].

Cavalcanti et al. [31] investigated the adsorption of wastewater contaminants from petroleum refineries by organoclay and was able to eliminate highly toxic organic elements, such as mixtures of benzene, toluene, and xylene and phenols. Alardhi et al. [32] verified a matched pair method using ozone with activated carbon (AC) for refinery wastewater processing and accomplished a powerful COD elimination (90%) [32]. An additional new investigation applied adsorption after the biological treatment for dyeing and COD removal from wastewater, with 96% COD removal [32-34].

Activated carbon has traditionally been employed as an adsorbent to remove oil [35]. Due to the high cost of activated carbon for oily wastewater treatment and difficult regeneration [36], many researchers have looked at the possibility of employing less expensive materials as substitutes in recent years [37].

The rapid increase of research interest in this subject has been fueled by the introduction of low-cost adsorbents, such as anthracite, silica, metal oxides, coal and others materials: mineral clays, sediments, and soils. Anthracite is an excellent precursor for a variety of carbon compounds, including activated carbons, due to its structural order, high ultra-microporosity per volume, and low cost [38]. In addition, it is more readily available than other adsorbents.

It has been shown to be effective as an absorbent in a variety of applications, including the removal of both organic and inorganic contaminants from wastewater such as Mn (VII) and Cr (VI) [39], quinoline [40], and phosphate ion [41]. Indeed, the removal efficiency of phosphate and quinoline is respectively 85% and 97% [41, 42].

This research aims to investigate the effectiveness of anthracite in reducing the concentration of chemical oxygen demand (COD) and hydrocarbon organic pollutants from petroleum refinery effluents and studies on adsorption equilibrium and kinetics.

2 Material and Methods

2.1 Wastewater Sampling and characterization

Wastewater sampling was carried out on december 2nd, 2021 from Algiers refinery, These samples were taken from the company's general wastewater collection manhole before it was discharged into the sewerage network. The sample is stored in sealed bottles and transported to the laboratory under refrigerated conditions in the dark before usage to avoid changes in its physico-chemical properties. All parameters that can be changed are analyzed in the laboratory quickly as feasible using conservation guidelines and defined analysis procedures. 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 determination of total suspended solids was based on the gravimetric method. Pb, Cu, Zn, total Cr, Cd, and Fe, using an atomic absorption spectrophotometer (AAS) (AA 240FS Agilent, USA). The hydrocarbon composition was determined by gas-chromatography analysis with a flame ionization detector [43]. The chemical oxygen demand (COD) was determined spectrophotometrically by using a Merck COD cell test (HACH DR/1900) [43].

2.2 Adsorbent

In this work, anthracite was employed without any chemical processing. Before usage, 100 g of anthracite was crushed, powdered, sieved through a 1.5 mm sifter, and dried in an oven at 120°C for 2 hours.

The adsorbent was stored in sealed glass containers after drying. Table 1 shows the physiochemical features of anthracite. It contains more than 90% of Carbone. The particle size is less than 1.6 mm. The ash content of our adsorbent was 3%. The chemical composition of the anthracite was investigated by Energy Dispersive Spectroscopy (EDS, X-MaxN, UK). The crystalline phase was determined via X-ray diffractometry (Panalytical: XPERT-PRO with a ceramic monochromator and copper anticathode). Scanning electron microscopy (SEM) (Joel Jem 100B) is used to image the surface characteristic. A Shimadzu spectrometer was used to perform Fourier-transformed infrared spectroscopy (FT-IR), with wave numbers ranging from 400 to 4000cm^{-1}.

Table 1. Anthracite physicochemical properties

Property	**Composition**
Particle size	0.6-1.6 mm
Density	1.4 g/cm^3
Carbon content	$>$ 90%
Ash content	3%
Ignition loss	97.6%
Volatile matter	8%
Sulfur content	0.8%

2.3 COD and hydrocarbons batch adsorption

Batch adsorption equilibrium tests were conducted by contacting a specified amount of adsorbent (between 1 and 3.5g) with a 50mL refinery effluent sample in a sealed glass container with a known initial COD and hydrocarbons concentration. For different times at constant temperature, this was swirled at 800 rpm for 80 minutes using a magnetic stirrer. Samples were taken at regular intervals, and COD and hydrocarbons were analyzed.

Experiments were carried out at various times utilizing the previously described system to assess the effect of both contact time and adsorption kinetics.

To test the effect of adsorbent mass, a variety of anthracite masses ranging from 1 to 3.5 g were added to a set of glass tubes containing a certain volume of effluent.

In addition, the experiment was carried out by varying temperatures (298, 308, and 318 K) and pH levels to see how these affected the results. The pH of the solution was carefully adjusted to a range between 2 and 10 during the tests by adding volumes of HCl (0.1 mol/L) or NaOH (0.1 mol/L) solution and measuring it using a pH meter (S20, Mettler Toledo).

The following formulas (equations 1 and 2) were used to calculate the COD and hydrocarbon removal percentages, as well as adsorption at equilibrium:

$$R(\%) = \frac{C0 - Ge}{CD} 100 \tag{1}$$

and

$$ge = \frac{\mathrm{C0} - \mathrm{Ce}}{m} V \tag{2}$$

where R (%) is the removal percentage, C0 (mg/L) is the COD and hydrocarbons concentration in the raw wastewater, Ce (mg/L) is the COD and hydrocarbons concentration after adsorption, qe (mg/g) is the amount of maximum organic matter adsorbed per unit mass by the anthracite, V (L) is the volume of the wastewater, and m (g) is the anthracite weight.

3 Results and discussion

3.1 Characterization of the refinery wastewater

Table 2 shows the basic composition information of the refinery effluent. The Algerian guidelines establishing the limitations for industrial liquid effluent emissions [44] are frequently exceeded for various characteristics. For example, the content of suspended solids is 280 mg/L, the concentration of hydrocarbons is approximately 188 mg/L, the BOD_5 and COD values are 183 and 268 mg/L respectively. These high values could be explained by the abundance of oxidizable and organic matter in the effluents. For the mineral elements, there is a very low concentration of metals (0.022 mg/L for chromium and less than 0.01 mg/L for lead). The pH of wastewater is weakly basic (8.1). Electrical conductivity of our wastewater is 192 μs/cm. This value would be linked to the temperature of the waters and their mineral load following their passage through the neutralization pit.

In light of all of these findings, it can be said that the refinery wastewater is complex matrices of organic pollutants; because of this, The biodegradation of these materials results in an energetic consumption of dissolved oxygen, resulting in eutrophication of the receiving medium, deterioration of fauna and flora, and the emergence of dangerous resistant species.

3.2 Anthracite Characterization

Fig. 1 shows an FT-IR spectrum with anthracite distinctive bands. C-O and C-O-C stretching were assigned bands in the 1000–1300 cm^{-1} range [45, 46]. The peak at 1600 cm^{-1} belongs to C=C/C=O vibration. Even

Table 2. Physicochemical analysis of the refinery wastewater

Parameters	Unit	Values	Algerian Standard
Temperature	°C	28	35
pH	-	8.1	5.5-8.5
Conductivity	mS/cm	0.1928	-
Hydrocarbons	mg/L	188	10
Turbidity	NTU	680	-
Suspended matter	mg/L	280	30
COD	mg/L	268.5	120
BOD_5	mg/L	183	30
Cr	mg/L	0.022	0.5
Pb	mg/L	< 0.01	0.5

in high purity anthracites (purity ¿ 97%), oxygenated groups can be found in amorphous carbon sites [38]. Some bands in the 900–675 cm-1 range can be attributed to the inorganic oxide such as silicon oxide or iron oxide and out-of-plane C-H bonds and to the aromatic structure; whereas 3400 cm-1 is attributed to hydroxyl groups (O-H). This hydroxyl function could belong to an alcohol, phenol or carboxylic group.

The amorphous structure of anthracite is shown in an X-ray diffractogram (Fig. 2), it indicates that graphite, carbon, and quartz are present in the adsorbent.

The morphological structure and properties of the anthracite have been characterized by SEM analysis, and the images are presented in Fig. 3 at a resolution of 20 μm and 1 nm. It can be seen a rough surface and inhomogeneous pore distribution with different sizes, shapes and ruptures because of the impact process of coalification where the surface of anthracite contains amorphous phases [47]. The images also reveal that the outer surfaces are full of cavities which suggest that the supports have a large specific surface area. Fig. 4 shows the EDS spectrum of anthracite; we can note the presence of nitrogen, and sulfur in addition to the main constituent 84% carbon, 10% azote, 5% oxygen, and amorphous phase.

3.3 Results of elimination of COD and hydrocarbons by adsorption on anthracite

3.3.1 Effect of anthracite dose

The adsorbent dose is a crucial factor in the adsorption process. The studies are conducted at 25∘C with various dosages of anthracite at the initial pH after 3 hours of agitation. Fig. 5 presents the effects of different doses of anthracite concerning the COD and hydrocarbons removal percentages. The elimination percentages of pollutants increase quickly from 76 to 88% for hydrocarbons and from 50 to 68% for COD when the dose of anthracite is increased from 1 to 2.5 g; afterward, the removal percentage of COD and hydrocarbons increases gradually to 73 and 90% when the mass of anthracite is raised to 3 g. Beyond this mass, the percentage of elimination of pollutants remains practically constant. This could be because as the anthracite dose increases, the number of active sites and surface areas increase, favoring COD and hydrocarbon elimination. So, 3.0 g of anthracite is the optimized amount of adsorbent and is used for the remainder of the research. On the other hand, as the adsorbent dose increase from 3 to 3.5 g, there is not significant increase in percent removal. A mass above 3.5 g results in a drop in % removal.

3.3.2 Adsorption Kinetics

The definition of adsorption percentage mechanisms, which will drive absorption efficiency and prospective application of an adsorbent, is heavily influenced by adsorption kinetics. The adsorption percentage of COD and hydrocarbons was measured by contacting refinery effluent samples with a 3 g adsorbent dosage. As indicated in Fig. 6, the majority of the COD and hydrocarbons decrease occurs over the first 120 minutes. Following that, the COD and hydrocarbons concentrations remained nearly unchanged, indicating that the equilibrium amount had been reached.

Pseudo-first-order and pseudo-second-order models were used to assess data from batch kinetic studies in this work.

The pseudo-first-order model [48] is written as follows (equation 3):

$$\frac{dqt}{dt} = k(qe - qt) \tag{3}$$

The integrated form of the pseudo-first-order model is written according to the equation 4 :

$$\ln(qe - qt) = kt + \ln ge \tag{4}$$

qe (mg/g) : the quantity of COD and hydrocarbons adsorbed at equilibrium,

qt (mg/g) : the amount of pollutants adsorbed at time t,

k (1/min) : the rate constant for pseudo-first-order adsorption.

The straight line of ln (qe − qt) versus t can be used to calculate k and qe. The pseudo-second-order model [49] is written according to the equation 5 :

$$\frac{dqt}{dt} = k(qe - qt)^2 \tag{5}$$

The pseudo-second-order model has the following integrated form shown in equation 6 :

$$\frac{t}{q} = \frac{I}{qe^2 k} + \frac{t}{qe} \tag{6}$$

The amount of COD and hydrocarbons adsorbed at equilibrium is qe (mg/g), and the pseudo-second-order constant is k (g/mg min).

The slope and intercept of the plot of t / q versus t, can be used to calculate qe and k respectively. According to the linearized Lagergren's pseudo-first-order equation (Eq. 4), the relationship between ln (qe-qt) and t is illustrated in Fig. 7. We notice that the pseudo-first-order equation offered a poor match to the experimental data. When plotting t/q versus t using the linearized pseudo-second-order model (Eq. 6), a clear linear relationship was detected in all situations, as shown in Fig. 8; straight lines fitted the data perfectly well, with R^2 values of 9.99. This demonstrates that the pseudo-second-order model adequately describes the adsorption kinetics. The model's kinetic parameters are listed in Table 3.

To understand the mechanism of adsorption of the pollutants on the anthracite, we applied the kinetic model of intra-particle diffusion (Weeber and Morris) [50] in the case of internal diffusion to justify the determining step of the mechanism (equation 7) :

$$qt = kt^{1/2} \tag{7}$$

The graph qt = f ($t^{1/2}$) represented by Fig. 9 is not a straight line passing through the origin. Therefore, the intraparticle diffusion kinetic model is not limiting for the mechanism, other mechanisms can be involved in the adsorption phenomenon, which are film diffusion, surface adsorption, and finally diffuse into the porous structure of the adsorbent and a monolayer forms on the surface.

Table 3. Regression data from kinetic models

Kinetic models	**Pseudo-first-order**		**Pseudo-second-order**		
	COD				
Parameter	R^2	ge (mg/g)	R^2	ge	k (g/mg min)
R^2	0.940	-	0.999	-	-
ge (mg/g)	-	-	-	20.5	-
k (1/min)	-	-	-	0.072	-
	Hydrocarbons				
Parameter	R^2	ge (mg/g)	R^2	ge	k (g/mg min)
R^2	0.8716	-	0.9956	-	-
ge (mg/g)	-	-	-	17.21	-
k (1/min)	-	-	-	0.084	-

3.3.3 Effect of pH

The effect of initial pH on the adsorption of COD and hydrocarbons was investigated at room temperature for different initial pH values in the range of 2–10. It's worth noting that the pH of refinery wastewater was typically around 8. The equilibrium uptake as a function of pH is shown in Fig. 10. Although there was a minor increase, especially for the adsorption of hhydrocarbons, for pH values ranging from acidic to basic media, the reduction percentage varies from 83% in very acidic medium (pH = 2) to 91% in basic medium (pH = 10) for COD and from 92% (pH = 2) to 94% (pH = 10) for hydrocarbons. This observation comes from the fact that the surfaces of the anthracite and the hydrocarbons are not charged. Therefore, changing the hydrogen ion concentration should have minimal effect on the adsorbent- hydrocarbons interaction. However, at very high pH values, there was an increase in adsorption performance (case of COD). This can be explained by the fact that increasing the pH induces the deprotonation of the OH functional group on the surface of the adsorbent and improves the π electron donor capacity of the surface and thus enhances the π-π donor interactions of electrons – aromatic acceptor. The adsorption of COD on date-pit activated carbon yielded similar results for the optimum pH range [51].

3.3.4 Effect of Temperature

Measuring the residual concentrations of COD and hydrocarbons in the refinery wastewater at different temperatures (25, 35, and 45°C) and different initial concentrations of the pollutants studied made it possible to establish the curves of the adsorption isotherms onto anthracite. Figs. 11 and 12 reveal a multilayer profile, which is likely due to limited porosity and a lack of adsorption sites on the adsorbent surface. The maximum adsorption capacity is observed at a temperature of 45°C 5.8 mg/g against 5.1 mg/g at 35°C and 4.7 mg/g at 25°C for hydrocarbons and 14 mg/g to 7 mg/g for COD.

Furthermore, increasing the temperature improves the adsorption capacity; this shows that as the temperature raises, the mobility of organic matter increases, allowing enough energy to interact with active sites on the surface of anthracite. This pattern points to a chemisorption reaction involving valence forces and electron sharing or exchange between organic matters and the adsorbent.

3.3.5 Modeling of the adsorption equilibrium

The linearization of the adsorption isotherms by using the equations (8 and 9) of the Langmuir [52] and Freundlich models [53], below, is presented in the figures 13 and 14.

$$\frac{I}{Qe} = \frac{1}{Qm} + \frac{1}{bQmCe} \tag{8}$$

$$\ln Qe = \ln K_F + \frac{1}{n} \ln Ce \tag{9}$$

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

Ce: concentration of solute at equilibrium (mg/L),

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

b: Langmuir constant (L/mg),

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

A comparison of the correlation coefficients "R^2" in table 4 shows that the Langmuir model presents the best fit of the experimental data, therefore a better adsorption of COD and hydrocarbons on the anthracite (R2 close to 1). This indicates that the retention of this compound occurs on a homogeneous surface and by monolayer adsorption. The numerical values of the constants of the two models applied (Qm, b, KF and n) calculated from the straight lines Qe =f(Ce) and 1/Qe =f(1/Ce), are shown in table 4.

Table 4. Determination of adsorption constants according to the Langmuir and Freundlich models

Adsorbate	**Langmuir Model**			**Freundlich Model**		
	Q_m (mg/g)	B	R^2	n	K_F	R^2
COD	6.666	0.023	0.9864	2.004	0.430	0.9536
Hydrocarbons	62.500	2.511×10^{-3}	0.9828	0.881	0.123	0.961

3.3.6 Thermodynamic Parameters of the Adsorption Equilibrium

The thermodynamics parameters, including changes in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS), are calculated using the adsorbed hydrocarbons quantities at equilibrium at 298, 308, and 318 K using the following formulae (equations 10 and 11) [54-55]:

$$\Delta G = -RT \ln Kd \tag{10}$$

T is the temperature in Kelvin (K), R is the constant of ideal gases (8.314 J / mole K).

The distribution ratio (Kd) was calculated using the equation below:

$$Kd = \frac{Cs}{Ce} \tag{11}$$

Cs is the concentration, at equilibrium, of the adsorbate on the surface of the anthracite; Ce is the equilibrium concentration in solution (mg/L).

The variations in enthalpy ΔH and entropy ΔS are calculated from equation (12):

$$\Delta G = \Delta H - T\Delta S \tag{12}$$

The slope and intercept of the linear plot of ΔG versus T are used to calculate ΔH and ΔS (Fig. 15).

The free energies ΔGvalues are negative in Table 5, indicating that organic material adsorption is spontaneous. A positive value ofΔH indicates endothermic adsorption, while a value of H greater than 40 kJ/mol

Table 5. Thermodynamic parameters for adsorption of organic materials from refinery wastewater on anthracite

T (°C)	**K d**	**ΔG** (J/mol)	**ΔH** (J/mol)	**ΔS** (J/mol · K)
25	1.44	-903.77		
35	4.6	-3909.54	58107	1991
45	6.34	-4884.96		

indicates chemical adsorption which includes strong electrostatic chemical bonding between pollutant and adsorbent surface [56]. The positive entropy change ΔS indicates an increase in unpredictability [57].

Table 6 shows the comparison of COD removal from refinery wastewater using others treatment methods. We note that our material adsorbent gave a very acceptable COD treatment efficiency of (82%) compared to other materials.

Table 6. Comparison of COD removal results with other refinery wastewater treatment methods

Treatment methods	**Removal percentage (%)**
Electro-Coagulation Process using SS/Al electrodes [58]	96.8%
Nanotitania Photocatalyst and UV Light Emission [59]	72%
Chemical Oxidation [60]	36-70%
Adsorption on date-pit activated carbon [51]	53%
Adsorption on functionalized mesoporous material with amine groups (NH2-MCM-41) [61]	40%-66%
Adsorption on activated carbon [62]	96.7%

3.3.7 Adsorbent regeneration tests

To assess the reuse of the system, regeneration tests were carried out. The regeneration of the adsorbent used for a new elimination of the pollutants was tested by means of batch processes. The HCl at 5% has been tested. As shown in Fig. 16, COD and hydrocarbons can be effectively removed. Anthracite regeneration was evaluated over 5 successive regeneration cycles and the COD and hydrocarbons adsorption percentage decreased after 5 adsorption-desorption cycles from 75% to 39% and 87% to 49% respectively.

4 Conclusion

The physico-chemical characterization of the refinery wastewater showed a considerable organic pollutant load (COD: 268.5 mg/L, BOD5: 183 mg/L, and hydrocarbons 188 mg/L). So the treatment of these waters is essential. The use of inexpensive natural adsorbent anthracite, which is one of the coals with the highest number of carbon and contains the least amount of impurities, to reduce the concentration of hydrocarbons and the COD of this effluent by the adsorption technique is investigated in this study.

The results of the adsorption of the two pollutants studied (COD and hydrocarbons) on anthracite have shown that the optimal mass of the adsorbent is 3 g with a treatment efficiency of 82% for COD and 94% for hydrocarbons. The retention speed is slow (120 minutes of contact time) and is of the pseudo-second-order type. A high temperature favors the absorption of the compounds; the adsorption process is endothermic and spontaneous. Adsorption isotherms on anthracite fitted the Langmuir model well. Finally, starting from the variation of the influencing factors and the effectiveness of the treatment, Application of anthracite as an adsorbent in real environmental water samples confirmed its effectiveness and efficiency, and consequently the relevance of this study. This material shows excellent promise for the simple, fast and good adsorption capacity of pollutant from wastewater. We could make a forecast of the choices and the conditions of realization at a higher level and thus recommended for control of aqueous polycyclic aromatic hydrocarbon pollution.

5 Declaration of Competing Interest

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of the article.

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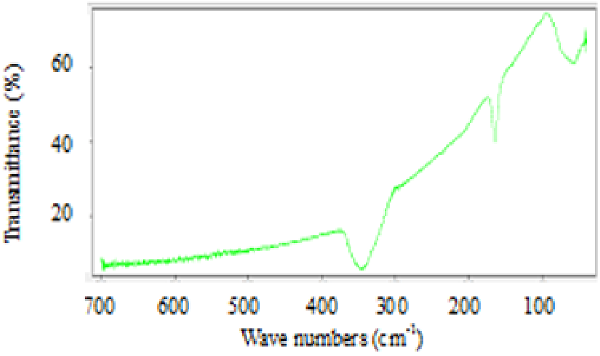

Fig. 1. FTIR spectrum of anthracite coal

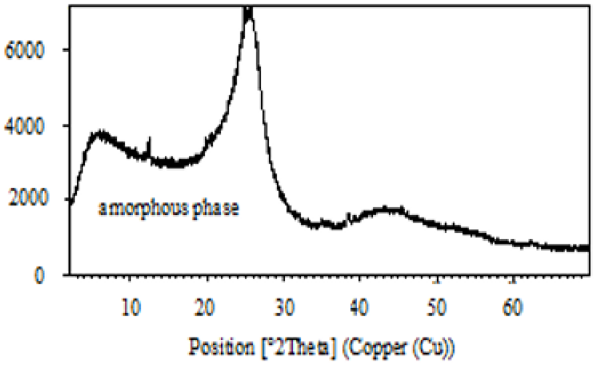

Fig. 2. X-ray diffractogram of anthracite

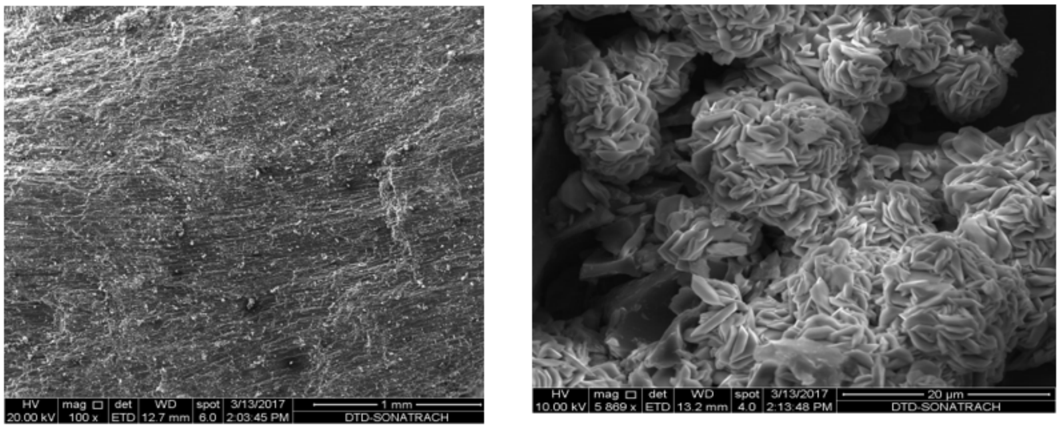

Fig. 3. SEM micrographs of anthracite

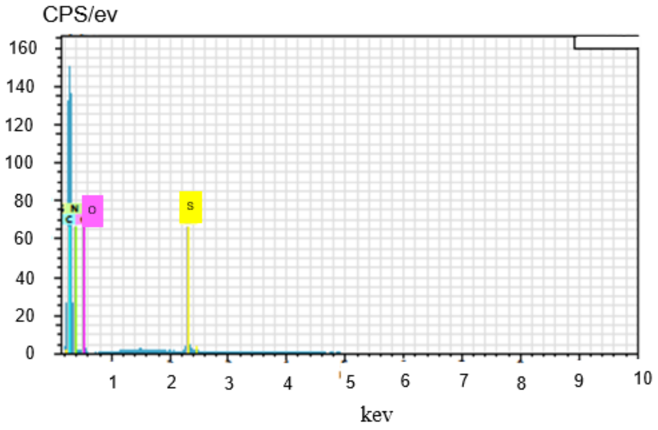

Fig. 4. EDS spectrum of anthracite

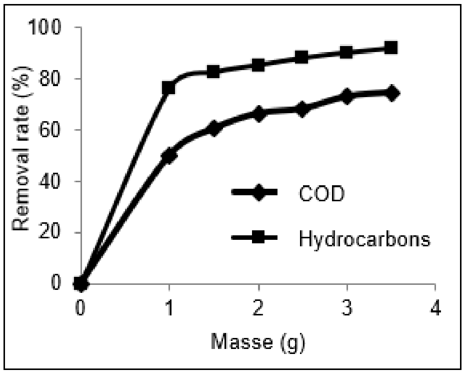

Fig. 5. Effect of anthracite dose on COD and hydrocarbons removal rate

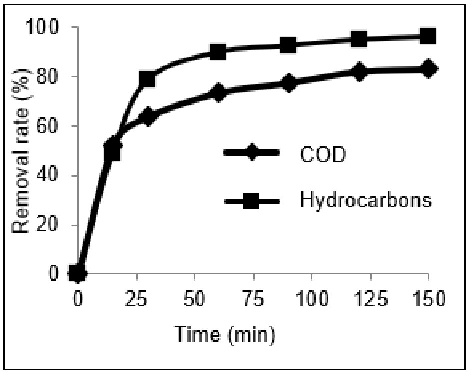

Fig. 6. Sorption kinetics of organic materials extraction from petroleum wastewater by anthracite

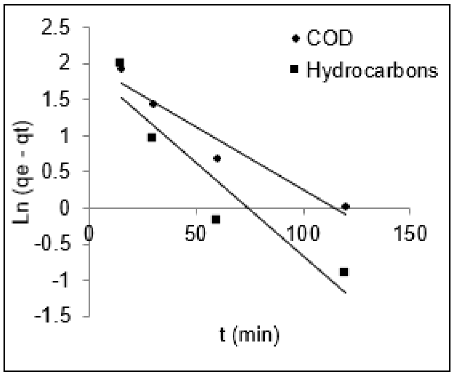

Fig. 7. Adaptation of experimental data on COD and hydrocarbons adsorption onto anthracite using pseudo-first-order equation

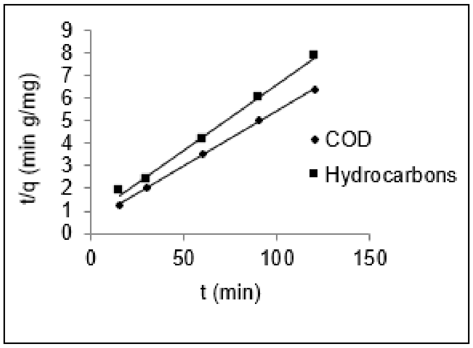

Fig. 8. Adaptation of experimental data on COD and hydrocarbons adsorption onto anthracite using pseudo-second-order equation

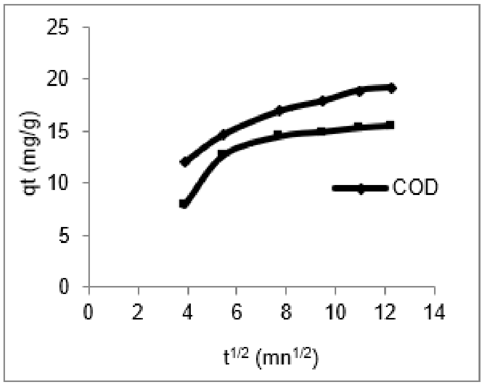

Fig. 9. Model of intra-particle diffusion

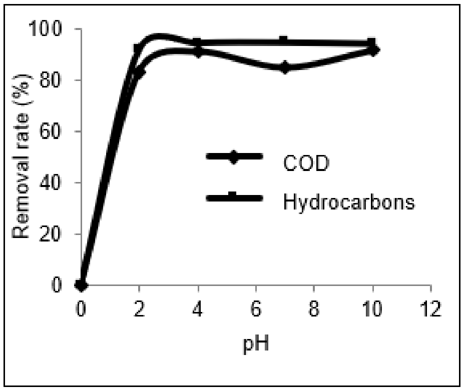

Fig. 10. Equilibrium isotherm data for the adsorption of COD and hydrocarbons at different pH values

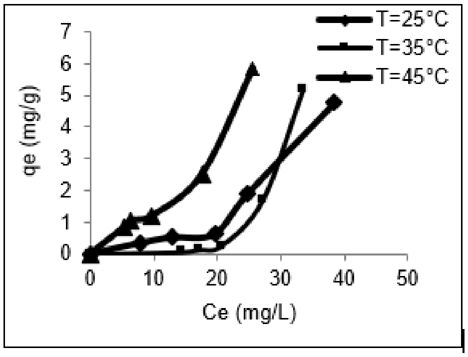

Fig. 11. Adsorption isotherms of hydrocarbons onto anthracite at different temperatures

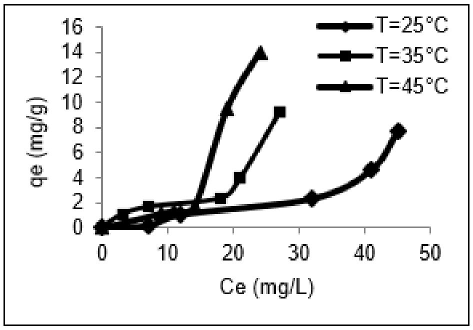

Fig. 12. Adsorption isotherms of COD onto anthracite at different temperatures

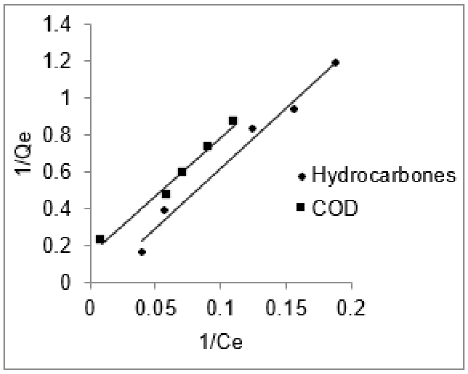

Fig. 13. Modeling of the adsorption isotherms of COD and hydrocarbons on anthracite according to the Langmuir equation

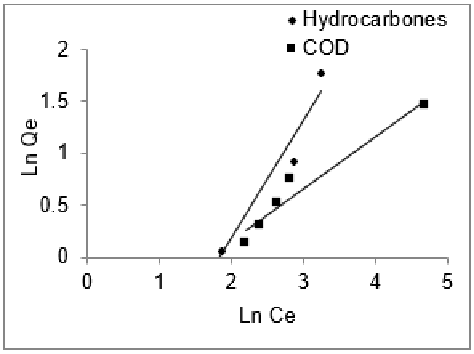

Fig. 14. Modeling of the adsorption isotherms of COD and hydrocarbons on anthracite according to the Freundlich equation

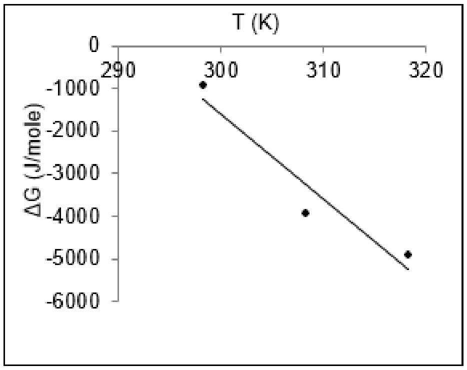

Fig. 15. Variation of Gibbs free energy as a function of temperature (Case of hydrocarbons)

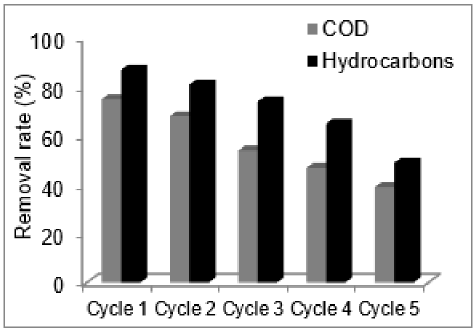

Fig. 16. Performance of anthracite after 5 cycles of adsorption-desorption of COD and hydrocarbons

Biographies

Mounir ZIATI

Mounir ZIATI is currently a Professor in the department of Chemistry, faculty of Sciences at M'hamed Bougara University of Boumerdes in Algeria. Member of laboratory of Soft Technologies, Physicochemical, Valorization of Biological Materials and Biodiversity, and Laboratory of Applied Chemistry and Materials of the University of Boumerdes (Algeria).

Pr. ZIATI received his undergraduate degrees as well as his PhD degree from Badji Mokhtar University of Annaba-Algeria.

Pr ZIATI published a number of papers in proven Journals, and participated in several national and international conferences. His main interests included environmental decontamination particularly water and soil, by eliminating pollutants using various physicochemical, electrochemical or biological processes.

Sara Khemili

Sara Khemili is currently member of laboratory of Soft Technologies, Physicochemical, Valorization of Biological Materials and Biodiversity of the University of Boumerdes (Algeria), preparing her research work as part of her doctoral thesis.

Khemili received his undergraduate degrees from Houari Boumedienne University of Sciences and Technology of Algiers-Algeria.

Khemili participated in several national and international conferences. Her main interests included the preparation of materials and their use in wastewater treatment.

Aicha METALI

Aicha METALI is currently member of laboratory of Soft Technologies, Physicochemical, Valorization of Biological Materials and Biodiversity of the University of Boumerdes (Algeria), preparing her research work as part of her doctoral thesis.

She received herMaster in Chemistry from Houari Boumedienne University of Sciences and Technology of Algiers-Algeria.

Metali participated in several national and international conferences. She is presently workings on decontamination of industrial sludge by the electrokinetic process.