Chapter 18
Adsorption of Inorganic and Organic Pollutants in Urban Wastewater Treatment Using Pine Wood Activated Carbon

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Abstract Water pollution is a physical, chemical, biological or bacteriological degradation of its natural qualities, caused by man and his activities. Also is caused by the discharge of water soiled by our domestic activities (washing and cleaning, evacuation of our urine and faeces, etc.) or by the various industrial and agricultural activities, necessary to provide the food and goods we need. During this work, we focused on reducing the abatement rate of urban wastewater by adsorption method using commercial activated carbon. Different experimental parameters were analyzed: contact time and adsorbent mass. The experimental results made it possible to determine the contact time and the optimal mass of activated carbon for BOD_5, COD and TSS ($t = 180$ min and $m = 1$ g). Kinetic study results show that equilibrium is established after 180 min and that the pseudo-second-order model describes our absorption phenomenon well.

Keywords Adsorption · Organic and inorganic pollutants · Urban wastewater

18.1 Introduction

Wastewater treatment plants are the receptacle for a very wide variety of wastewater to be treated. They can be from domestic, industrial or craft activities and from health care activities. These effluents contain numerous chemical substances, some of which are qualified as "micropollutants" because they are present in very low concentrations, in the order of nanograms to micrograms per liter. Micropollutants are inorganic or organic molecules that can have negative impacts on ecosystems and

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the environment. These micropollutants can contain toxic elements that are harmful to health, leading to the damage of the quality of water resources (Samuel 2010). And for the preservation of the latter, the discharge of wastewater must be authorized by the AHBT (Agency of the hydraulic basin of Oued Tensift) as stipulated in the law n°36–15 fixing the limit values of rejection to respect (Haytem and Boumenkar tarek 2019). The protection of the environment includes all measures to safeguard the health of humans, animals and plants, preventing any pollution or alteration of the air, soil, surface and groundwater and avoiding the defacement of the landscape (Reporterre 2020). In a world where the demand for freshwater is steadily increasing, and where limited water resources are increasingly under stress from overexploitation, pollution, and climate change, it is simply unthinkable to overlook the opportunities that improved wastewater management offers. This is the conclusion of the World Water Development Report 2017, which highlights the critical importance of improved wastewater management to our shared future. To maintain our current habits is to encourage the worsening of already considerable neglect (WWAP 2017; Crini et al. 2007). European regulations, in particular through the Water Framework Directive (Directive 2000/60/EC or WFD) and the latest Directive 2013/39/EU, defines a list of 45 priority substances for which environmental quality standards must be respected. Environmental quality standards must be met. These substances include trace metals (TMEs) and trace organic compounds (TOCs). To date, Morocco has established a policy based on the participation of the representatives concerned to monitor the emissions of micropollutants in the natural environment and in the wastewater treatment plants (WWTP). For this reason, Morocco has decided to commit itself to carry out numerous studies to get an idea of the nature of the micropollutants found in surface waters or discarged from wastewater treatment plants (WWTPs). To this end, to monitor water quality, adequate instruments have to be developed. In addition, the treatment processes must be improved to treat the micropollutants found (Demirbas 2009; Bliefert and Perraud 2001). The adsorption technique is the most favorable method for the removal of inorganic and organic pollutants. It has become the analytical method of choice, very efficient and simple in its use (Azoulay et al. 2021). The principle of adsorption treatment is to trap pollutants in solid materials called adsorbents. In the literature, there are several solid materials (biomass, polymer, activated carbon, sludge, waste agricultural…) that can be used in wastewater removal processes (Bencheikh et al. 2021). The present study deals with the reduction of the abatement rate of urban wastewater by the adsorption method using activated carbon prepared from raw material (pine wood).

18.2 Materials and Methods

18.2.1 Materials

Preparation and characterization of activated carbon AC. Activated carbon (AC) is considered a reference material in water treatment due to its ability to remove a wide range of inorganic and organic pollutants. The activated carbon (AC) used in this study was recovered from LABOSI, France. It is prepared from the raw material (pine wood) but has undergone different treatments to acquire the properties described in Table 18.1.

Physico-chemical characteristics of urban wastewater. We chose purified water generated from an urban wastewater treatment plant to reduce the physico-chemical parameters by the adsorption method as a finishing method. Table 18.2 shows the physicochemical characteristics of raw and treated water on which the adsorption experiments will be performed.

Table 18.1 Characteristics of activated carbon used in our study (supplier data)

Properties	Carbon
Vendor	LABOSI, France
Particle size	~40 µm
BET specific surface	1050 $m^2\ g^{-1}$
Raw material	Pinewood
Activation	Physics
Character	Basic
C in %	84.2
H in %	1
N in %	0.6
O in %	1.77

Table 18.2 Physico-chemical characterization of raw and purified water on which the adsorption experiments will be performed (Mabrouki et al. 2022)

Parameters	Raw water	Purified water	Standard Moroccan (Mabrouki et al. 2022)	Discharge Limit Values (Mabrouki et al. 2022)	
				Direct	Indirect
pH	7.91	7.89	5.5–9.5	6.5–8.51	6.5–8.51
T (°C)	21	20	30	30	35
TSS (mg/L)	690	325	150	50	600
COD (mg O2/L)	907	482	250	500	1000
BOD_5 (mgO2/L)	480	220	120	100	500

18.2.2 Experimental Methods

Determination of the hydrogen potential (pH). The pH was measured using the HACH model Sension 2 portable pH meter, with automatic temperature compensation. Before each measurement, a systematic calibration of the apparatus was carried out (accuracy ± 0.01).

Determination of the temperature. The temperature in °C was measured using a portable EUTECH instruments probe (Fisher Bioblock, France).

Determination of Chemical Oxygen Demand (COD). The organic pollutants were determined globally by COD measurement. The principle of this determination is based on the oxidation by an excess of potassium dichromate in an acid medium and boiling of the oxidizable materials contained in the aqueous solution analyzed, in the presence of silver sulfates as catalyst and mercury sulfate as complexing agent (Mabrouki et al. 2019).

Determination of the Biological Oxygen Demand after 5 days (BOD_5). The Biochemical Oxygen Demand determines the amount of oxygen, expressed in milligrams, that is consumed under the test conditions (incubation for five days, at 25 °C and in the dark) by certain materials present in a litre of water, in particular, to ensure their degradation (Mabrouki et al. 2019). The principle of this determination is based on the oxygen consumption of the medium under study compensated by a supply of pure oxygen. The measurement of the quantity of oxygen with time corresponds to the Biochemical Oxygen Demand of the medium under the given conditions. The measurement of COD and BOD_5 is carried out by a HACH-type oximeter model HQ10.

Suspended solids (SS). Total Suspended Solids (TSS) presents the amount of organic and inorganic pollutants and mineral pollutants not dissolved in water (EMabrouki et al. 2021). It is determined by quantitative analysis gravimetric method) according to the standard NF EN 1234-June 2014. For this purpose, a volume V (200 ml) of the water sample to be analyzed is taken and poured onto a previously weighed filter paper (M1). This filter paper containing the sample is then introduced into the oven at 105 °C for a period varying between one hour and two hours until total evaporation of the water and is then cooled in a desiccator for 20 min to 60 min and then weighed again (M2). Results are expressed in mg/l (Eq. *18.1*).

$$TSS = (M1 - M2) \Big/ V * 1000 \tag{18.1}$$

Experimental batch adsorption. The adsorption experiments of the pollutants contained in water by activated carbon CA were carried out in the "batch method" in Erlenmeyer flasks of 100 ml, at room temperature (30 ± 2 °C) and a stirring speed of 300 rpm. The effects of contact time and activated carbon mass were studied. After a contact time long enough to reach equilibrium, the solutions were filtered through Double Rings Filter Paper and the aqueous solution was analyzed for residual pollutant concentration. The removal efficiency was calculated according to Eq. (*18.2*):

$$R = \frac{C_i - C_e}{C_i} * 100 \tag{18.2}$$

C_i: Initial concentration of the organic compound tested (mg/L);
C_e: Concentration of organic compound tested at equilibrium (mg/L).

Influence of contact time. The experimental procedure followed consists of putting 1 g of powdered activated carbon in contact with a series of identical flasks each containing 250 ml of purified water at a given initial concentration. The whole is maintained in constant agitation at room temperature. At regular intervals, the content of one of the vials is emptied, filtered and the solution analyzed, and so on until the last vial. The content of adsorbed pollutants at each time Qt (mg/g) was calculated by the Eq. 18.3:

$$Q = \frac{C_i - C_e}{m} * V \tag{18.3}$$

where:

C_0 and C_e (mg/L) represent the initial and equilibrium concentration in the solution, respectively;
V is the volume of the solution;
m is the mass of dry activated carbon used.

Influence of activated carbon dosage. The method consists in introducing in several Erlenmeyer flasks of variable masses of activated carbon, a volume (100 ml) of purified water. The whole is stirred under the same conditions for a period longer than the equilibrium time. At equilibrium, the solutions are filtered and the residual concentration of the pollutants is measured in the solution.

Description of the experimental procedure of adsorption kinetics. In the kinetic study of the adsorption of BOD_5, COD and TSS we take a volume of 600 ml of water discharged in a batch and a mass of 1.638 g of AC. Samples of the supernatant of the mixture (adsorbate/adsorbent) are taken every 10 min and filtered on Double Rings Filter Paper. The final concentration of BOD_5, COD and TSS is measured for each sample.

18.3 Results and Discussions

18.3.1 Evaluation of the Organic Pollution of Wastewater (Biodegradability)

Biodegradability reflects the ability of the effluent to decompose or oxidize Microorganisms involved in the biological water purification process (Metahri 2012). The

Table 18.3 Physico-chemical characterization of raw and treated water with the ratio COD/BOD_5

Parameters	Raw water	Purified water	Standard Moroccan (Mabrouki et al. 2022)	Discharge Limit Values (Mabrouki et al. 2022)	
				Direct	Indirect
pH	7.91	7.89	5.5–9.5	6.5–8.51	6.5–8.51
T (°C)	21	20	30	30	35
TSS (mg/L)	690	325	150	50	600
COD (mg O_2/L)	907	482	250	500	1000
BOD_5 (mgO_2/L)	480	220	120	100	500
COD/BOD_5	1.89	2.19	–	–	–
BOD_5/COD	0.53	0.46	–	–	–

value of the COD/BOD_5 ratio determines the choice of treatment approach. If the effluent is biodegradable, biological treatment should be applied. Otherwise, apply a physicochemical treatment (Mabrouki et al. 2018). We note that the estimation of the origin of the organic matter brought by the wastewater is done by the calculation of the average ratio COD/BOD_5. This COD/BOD_5 ratio also determines the degradability and expected yield of the biooxidative treatment (Table 18.3). The BOD_5/COD ratio provides very interesting information about the sources of wastewater loads and their treatment options (ISO 1994).

From Table 18.3 we observe that the ratio of COD/BOD_5 of the raw water, i.e. the inlet water, is between 1.5 and 2, so we can say that the effluent of the food industry is biodegradable. On the other hand, the ratio of COD/BOD_5 of the treated water, i.e. the outlet water, is between 2 and 3, so we can say that the predominantly domestic effluent is easily biodegradable. While the BOD_5/COD ratio is relatively high at about 0.53. This is the general case for emissions contaminated with organic matter. This organic load makes this effluent very unstable. It can quickly develop into a "digested" form that risks releasing odors. In fact, the effluent from this collector is mostly organic.

18.3.2 Parameters Effect

Influence of contact time on COD, BOD_5 and TSS removal. Figure 18.1 shows the evolution of the percentage of COD, BOD_5 and TSS abatement as a function of time at 30 °C for a solution of volume equal to 250 mL, containing respectively $[COD]0 = 220$ mgO_2/L, $[BOD_5]0 = 482$ mgO_2/L, $[TSS]0 = 325$ mg/L and a mass of 1 g of activated carbon.

The graphs in Fig. 18.1 show maximum adsorption at 180 min for BOD_5, SS and COD. We observe that the first phase of adsorption takes place in a few tens of minutes (80 min). Thus a second slower phase can last from 80 to 180 min. After

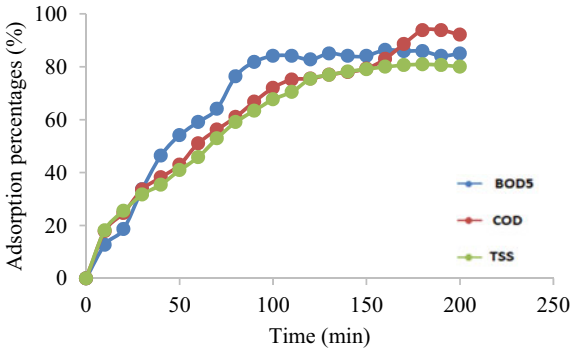

Fig. 18.1 Influence of contact time on COD, BOD_5 and TSS removal (V = 250 ml, m(AC) = 1.25 g, $[BOD_5]0 = 220$ mgO_2/L, $[COD]0 = 482$ mgO_2/L, $[TSS]0 = 325$ mg/L)

180 min, the effect of the contact time does not affect the adsorption capacity of COD, BOD_5 and SS, so the adsorption equilibrium is reached at 180 min.

Influence of activated carbon mass on COD, BOD_5 and TSS removal. Figure 18.2 shows the evolution of the percentage of COD, BOD_5 and TSS removal as a function of the mass of activated carbon used in the tests at 30 °C for a solution of volume equal to 250 mL, containing respectively $[COD]0 = 220$ mgO_2/L, $[BOD_5]0 = 482$ mgO_2/L, $[TSS]0 = 325$ mg/L and a contact time of 200 min.

The analysis of these results shows that the adsorption efficiency of COD, BOD_5, and TSS increases with the mass of the adsorbent to stabilize at a value close to 1.25 g of activated carbon. Many authors (Mabrouki et al. 2020) have shown that the percentages of adsorption increase with the mass of activated carbon used, reaching here more than 80% of COD, BOD_5 and TSS removal.

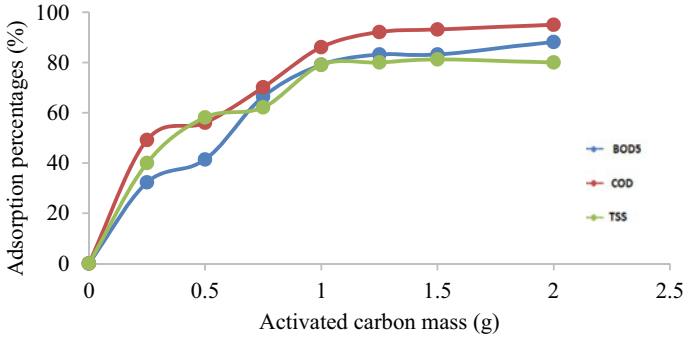

Fig. 18.2 Influence of commercial activated carbon dosage on COD, BOD_5 and TSS removal (V = 250 ml, t = 2 h, $[BOD_5]0 = 220$ mgO_2/L, $[COD]0 = 482$ mgO_2/L, $[TSS]0 = 325$ mg/L)

18.3.3 Adsorption Kinetics

The results obtained from these experiments showed the existence of two trends over time.

- A first rapid trend between 0 and 80 min. The adsorbed quantities reach 37, 50 and 90 mg/g respectively for BOD_5, TSS and COD after 80 min of contact.
- A second slow trend after 80 min. The quantities adsorbed gradually until equilibrium. This can be explained on the one hand by the decrease of the concentration gradients as the adsorption proceeds, which has a direct impact on the kinetics. On the other hand, it can be attributed to the high availability of active sites on the surface of the AC.

Indeed we also notice in Fig. 18.3 that the amount of COD adsorbed is higher than that of BOD_5 and TSS. This remarkable difference is explained by the high affinity of activated carbons for organic compounds and a medium affinity for certain inorganic compounds. However, the BOD_5 only takes into account organic compounds.

Furthermore, the removal kinetics of BOD_5, COD and TSS on activated carbon was examined using pseudo-first-order and pseudo-second-order kinetic models.

Figures 18.4 and 18.5 represent the plots of the kinetic models (pseudo-1st-order and pseudo-2nd-order) applied to study the kinetic results.

The different kinetic constants extracted from the plotting equations of BOD_5, COD and TSS adsorption on AC (see Figs. 18.4 and 18.5) are grouped in Table 18.4.

From Table 18.4, the pseudo-second-order model describes the experimental data well since the corresponding correlation coefficient ($R^2COD = 0.918$, $R^2BOD_5 = 0.9068$ and $R^2TSS = 0.9333$) is higher than the pseudo-first-order model. In addition, the experimentally determined value of Q_{exp} in the equilibrium tests is closer to that of Q_{cal} determined theoretically with the pseudo-2nd-order model than to Q_{cal} determined with the pseudo-1st-order model. These two conditions would indicate

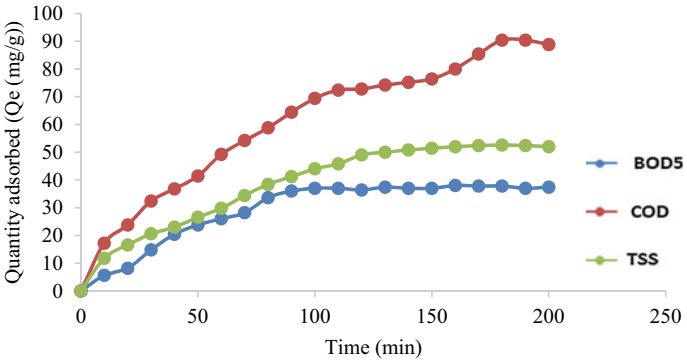

Fig. 18.3 The variation of the adsorbed quantity of BOD_5, COD and SS on AC as a function of time

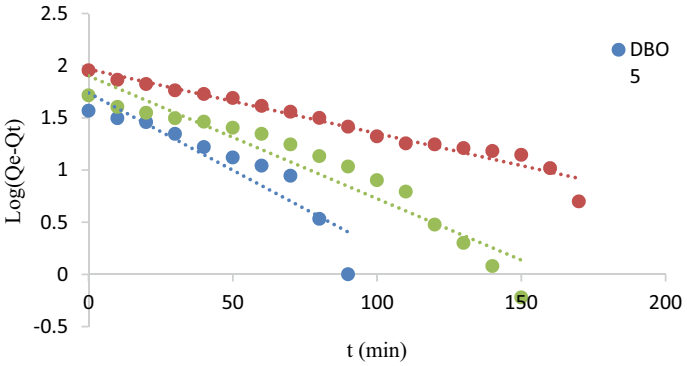

Fig. 18.4 Pseudo-1st-order kinetics model

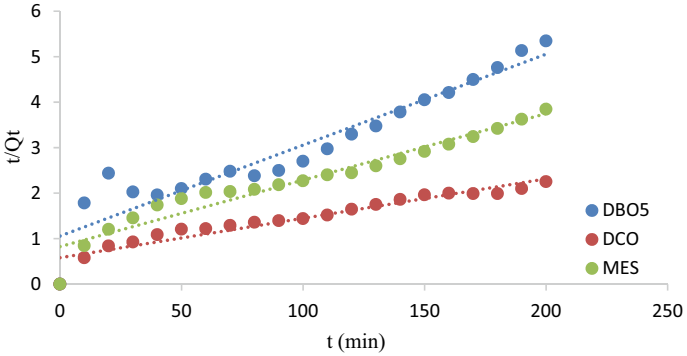

Fig. 18.5 Pseudo-second order kinetics model

Table 18.4 Kinetic constants of BOD_5, COD and SS adsorption on AC

Parameters	BOD_5	COD	TSS
Pseudo-1st-order: Log $(Q_e - Q_t) = \log Q_e - K_1 * t/2.303$			
R^2	0.8493	0.9003	0.9146
Q_{cal} (mg/g)	5.697	7.123	6.707
Q_{exp} (mg/g)	37	90	50
K_1 (min^{-1})	0.034	0.0143	0.027
Pseudo-2nd-order: $t/Q_t = Q_e/K_2 + 1/Q_e$			
R^2	0.9068	0.918	0.9333
Q_{cal} (mg/g)	40	114.94	68.49
Q_{exp} (mg/g)	37	90	50
K_1 (g, mg^{-1}, min^{-1})	$3.7.10^{-4}$	$1.3.10^{-4}$	$2.58.10^{-4}$

that the adsorption process is predominantly controlled by chemisorption (Azoulay et al. 2022; Bencheikh et al. 2020).

18.4 Conclusion

From this study, we can see that activated carbon is capable of retaining organic and inorganic matter in an aqueous medium. However, with a maximum adsorption capacity equal to 90 mg/g (for the adsorption of organic and inorganic pollutants estimated by global measurement of COD), 50 mg/g (for the adsorption of suspended solids TSS) and 37 mg/g for the adsorption of organic pollutants alone BOD_5). This work was carried out to determine the optimal conditions for the removal of BOD5, COD and TSS on AC, we were led to carry out a parametric study, in which we took into account the influence of important factors such as the contact time and the mass of activated carbon used. The study of the influence of the mass and the contact time allowed us to determine the optimal conditions for BOD5, COD and TSS, which are:

- To determine the optimal conditions for the removal of BOD_5, COD and TSS on AC, we were led to carry out a parametric study, in which we took into account the influence of important factors such as the contact time and the mass of activated carbon used. The study of the influence of the mass and the contact time allowed us to determine the optimal conditions for BOD_5, COD and TSS, which are:
  - Time = 180 min
  - masse = 1 g.

The results of the kinetic study showed that the equilibrium is established after 180 min and that the pseudo-second-order model writes well our adsorption phenomenon.

References

Azoulay K, Bencheikh I, Mabrouki J, Samghouli N, Moufti A, Dahchour A, El Hajjaji S (2021) Adsorption mechanisms of azo dyes binary mixture onto different raw palm wastes. Int J Environ Anal Chem 1–20. https://doi.org/10.1080/03067319.2021.1878165

Azoulay K, Bencheikh I, Moufti A, Dahchour A, Mabrouki J, El Hajjaji S (2022) Comparative study between static and dynamic adsorption efficiency of dyes by the mixture of palm waste using the central composite design. Chem Data Collect 27:100385. https://doi.org/10.1016/j.cdc.2020.100385

Bencheikh I, Azoulay K, Mabrouki J, El Hajjaji S, Dahchour A, Moufti A, Dhiba D (2020) The adsorptive removal of MB using chemically treated artichoke leaves: parametric, kinetic, isotherm and thermodynamic study, Scientific African, vol 9, July, e00509. https://doi.org/10.1016/j.sciaf.2020.e0050.

Bencheikh I, Azoulay K, Mabrouki J, El Hajjaji S, Moufti A, Labjar N (2021) The use and the performance of chemically treated artichoke leaves for textile industrial effluents treatment. Chem Data Collect 31:100597. DOI: https://doi.org/doi:10.1016/j.cdc.2020.100597

Bliefert C, Perraud R (2001) Chimie de l'environnement: air, eau, sols, dechets. De Boeck Universite

Crini G, Badot PM, Morin-Crini GT (2007) Les principales techniques d'épuration des eaux industrielles polluées : une revue récente des méthodes proposées dans la littérature : traitement et épuration des eaux industrielles polluées. Presse universitaire de franche-Comité, Paris, p 3

Demirbas A (2009) Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review. J Hazard Mater 167:1–9

ISO 5667/3 (1994) Qualité de l'eau et échantillonnage. Guide pour la conservation et la manipulation des échantillons (1994)

Labbaci Haytem et Boumenkar tarek, analyse des anomalies et redimensionnement de la STEP de la Wilaya de SKIKDA, mémoire de master, université Badji Mokhtar Annaba, Algérie (2019)

Mabrouki J, El Yadini, A, Bencheikh I, Azoulay K, Moufti A, El Hajjaji S (2018) Hydrogeological and hydrochemical study of underground waters of the tablecloth in the vicinity of the controlled city dump mohammedia (Morocco). In: International conference on advanced intelligent systems for sustainable development. Springer, Cham

Mabrouki J, Bencheikh I, Azoulay K, Es-Soufy M, El Hajjaji S (2019) Smart monitoring system for the long-term control of aerobic leachate treatment: dumping case Mohammedia (Morocco). In: International conference on big data and networks technologies. Springer, Cham, pp 220–230

Mabrouki J, Benbouzid M, Dhiba D, El Hajjaji S (2020) Simulation of wastewater treatment processes with Bioreactor Membrane Reactor (MBR) treatment versus conventional the adsorbent layer-based filtration system (LAFS). Int J Environ Anal Chem 1–11

Mabrouki J, Azrour M, Hajjaji SE (2021) Use of internet of things for monitoring and evaluating water's quality: a comparative study. Int J Cloud Comput 10(5–6):633–644

Mabrouki J, Fattah G, Al-Jadabi N, Abrouki Y, Dhiba D, Azrour M, Hajjaji SE (2022) Study, simulation and modulation of solar thermal domestic hot water production systems. Model Earth Syst Environ 8(2):2853–2862

Metahri, élimination simultanée de la pollution azotée et phosphatée des eaux traitées, par des procédés mixtes. Cas de la STEP Est de la ville de Tizi-Ouzou. P17, 20, 22, 27, 63, 72, 73 et 74 (2012)

Reporterre (2020) 227 activistes de l'environnement assassinés en 2020, un record [archive], sur Reporterre, le quotidien de l'écologie (consulté le16 septembre 2021)

Samuel BAUMONT (2010) Réutilisation des eaux usées épurées: risques sanitaires et faisabilité en Île-de-France, Institut d'aménagement et d'urbanisme de la région Ile-de-France

WWAP (Programme mondial pour l'évaluation des ressources en eau). Rapport mondial des Nations Unies sur la mise en valeur des ressources en eau (2017) Les eaux usées – Une ressource inexploitée. UNESCO, Paris, p 2017