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Effect of the mineralization on removing the humic substances by adsorption on activated carbon

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ABSTRACT

It is well known that the reactivity of chlorine with the humic substances results the formation of organohalogens in particular trihalomethanes suffering having chronic toxicity (mutagenic and/or carcinogen). These compounds, if they are formed no treatment can eliminated them. In this context, the aim of our work is to test the performance of powder activated carbon on removing the humic substances in the various mediums of mineralization. The adsorption testing is performed in batch by adopting different operating conditions. We thus evaluated various parameters relating to adsorption laws who will inform us about the retention capacity of the adsorbents with respect to humic substances of the water tested. The physicochemical characteristics of the water tested were also determined. The results have shown that the tested water is characterized by a more or less important mineralization and the quality varies from very good to poor. The adsorption tests showed that the removal of humic substances on carbon activated powder is more or less important, according to the mineralization of water. The yields obtained ranging 92.10%–100% with an equilibrium time vary from 30 to 240 min. According to all the results that we obtained, we also suggest that mineralization has notable influence on the adsorption process, either globally or through the mineral elements present. Similarly, the origin and nature of the humic material, the particle size and the distribution of pores adsorbents, as well as the physicochemical characteristics of the medium significantly affect the removal efficiency of humic substances. The effectiveness of these adsorbents and the increasing of adsorption capacity were clearly appeared through the exploitation of our results by the Freundlich and Langmuir isotherms.

Keywords: Humic substances; Mineralization; Adsorption; Powder activated carbon

1. Introduction

Humic substances constitute the most important majority of organic fraction in natural water, either 40% or 60%, sometimes 90% of dissolved organic carbon. In Algeria, the humic material can represent a significant portion of the organic load of surface water. They are generally constitute the most important category in these water with the concentrations >1 mg/L, and the proportion in the range of 40%–90% of total organic carbon. These compounds are responsible for the color of the water; possess properties of ion exchangers and complexing properties [1]. They can be a vehicle for the most of toxic substances (heavy metals, pesticides, etc.), also participate in the distribution system corrosion and clogging of resins and membranes. It follows that this type of organic compound often presents considerable potentials of chlorine reactivity, accompanied by the formation of halogenated organic compounds and in particular the trihalomethanes having chronic toxicity (mutagenic and carcinogenic effect) [2]. These compounds if they are formed no treatment can eliminated them. Eliminating the macromolecules humic type is not always be sufficient, whatever the effectiveness of treatments for clarification. It necessitates the optimal conditions often scarcely compatible with the practical operating conditions and treatment as well

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as with potability criteria [3]. It is important to mention that, using adsorption processes are often a preferable technique, complementary to the base chain. Since the adsorption is efficient in the retention and removal of soluble organic and inorganic compounds in water without be changed. In this context, our objective is to test the performance of powdered activated carbon (PAC) in the removal of humic substances in mediums of variable mineralization. Adsorption tests are carried out in a static reactor by adopting different operating conditions, such as contact time, variation of the mass of powder activated carbon and the variation of the initial content of humic substances. We will, therefore, evaluate various parameters relating to adsorption who will inquire us about the retention capacity of adsorbents overlooked the humic substances of the water tested. The physicochemical characteristics of the water tested were also determined.

2. Materials and methods

2.1. Sampling and dosage methods

The mineralized water used such as dilution mediums of humic substances are sampled from the eastern and southeastern regions of Algeria namely:

- Youkous water: It is a commercial water comes from Tibessa (eastern region of Algeria).
- Source water: It is located in Timgad (Batna) for the supply of drinking water in the region (eastern region of Algeria).
- Tap water: It is from Mohamed Khider University of Biskra (southeastern regions of Algeria).

The drilling water comes from Sidi Okba of Biskra City (southeastern regions of Algeria).

Different physicochemical parameters of mineralization water tested are determined by standard analytical methods, in the aim to determine the quality of that water [4]. Parameters are pH, conductivity, total hardness (TH), total alkalinity (TAC), sulfates and chloride. All these parameters are shown in Figs. 1–3.

2.2. Description of the dilution mediums

The stock solution of humic substances is prepared at 100 mg/L. The dilution medium is four different types of mineralized water initially exempt from all traces of organic matter. It is important to note that, the humic substances are used in the form of sodium humate; they are commercial of a high chemical purity and mark Aldrich. By comparison with the works of Thurman [5] and Croué [6] we can say that sodium humate tested has characteristics close to those of aquatic humic substances in particular fulvic acids.

2.3. Description of adsorption processes

The tests for adsorption to PAC were carried out in batch using glass beakers of 1 L. The agitation time varies from 2 to 3 h on electromagnetic agitators, then followed by centrifugation at 3,000 rpm during 60 min. It is important to note that PAC is mesoporous. It is from Riedel Haen chemistry laboratory, characterized by 20 mm of particle size and 658 m^2/g specific surface. The evaluation of yields (R) of humic substances is followed by the parameter R: $R = (1 - C_e/C_o) \times 100$, with C_o the initial concentration of humic substances (mg/L) and C_e the concentration of residual humic substances (mg/L), deduced from the calibration curve. The different steps and operating conditions were also adopted as follows:

- The first step is to determine the equilibrium time and optimal removal yields of humic substances to which we add 1,000 mg/L of adsorbent for 1 L of aqueous solutions of mineralized water of humic substances (10 mg/L).
- The second step is to see the impact of the change in mass of adsorbent on the removal efficiency (yields) of humic substances. The mass of PAC is from 0.5 to 2 g.
- The third step is to test the effect of the initial content of humic materials for each type of mineralized

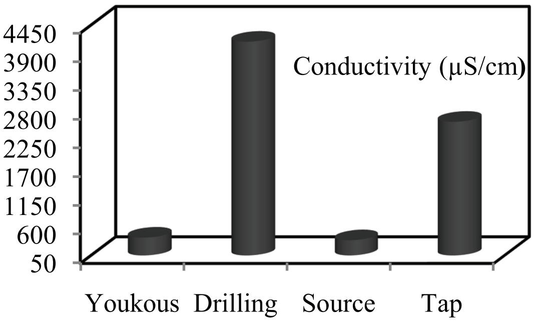

Fig. 1. Conductivity in the different waters tested.

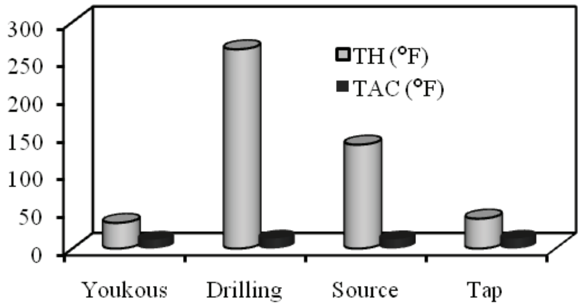

Fig. 2. Total hardness and the alkalinity in different water tested.

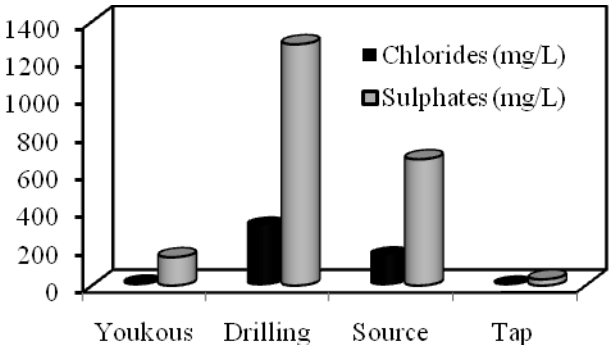

Fig. 3. Chloride and sulfate concentrationsin the different water tested.

water. The concentration range from 2 to 12 mg/L of humic substances for a fixed dose of adsorbent equal to 1,000 mg/L. In this step, we used the two isothermal laws by Freundlich and Langmuir.

For the last two steps, the stirring time is the equilibrium time determined in the first step.

3. Results and discussion

3.1. Quality of mineralized water tested

The results of the analysis physicochemical characteristics show generally that the temperature of our samples is between 12°C and 14°C; it is acceptable, because our work was done in the winter.

The pH is between 6.81 and 7.51. According to the World Health Organization (WHO) [7], the pH of drinking water must be between 6.5 and 9.20. Therefore, the pH of tested water is near neutral.

The water of the drilling and tap have a very high conductivity exceeding 1,000 μS/cm (Fig. 1). This conductivity causes an increase in salinity, the high conductivity may be either due to the nature of the geological layers of the ply, or due to the presence of the mineral elements resulting from exogenous pollution. While, the water of Youkous and source have less conductivity (1,000 μS/cm). They are weakly mineralized.

The TH (Fig. 2) shows that the water of tap and drilling are very hard. The TH greatly exceeds the norms of WHO [7]. This hardness is due to the dissolution of calcium and magnesium and essentially the infiltration of surface water through the rocks formations limestone and dolomite. These two types of water are very hard in comparison with the water of Youkous and source. The alkalinity of the water tested (TAC) is bicarbonate (Fig. 2) because the TH is always greater than the TAC and the pH of the water is <8.3. Through our results presented in Fig. 3, were recorded a high concentration of sulfates and chlorides in the water of tap and drilling, by comparison with the other two types of water. These two elements cause an unpleasant taste of water consumption and they are corrosive. They are also harmful for plants. Through our results, we can say that the water of tap and drilling are poor quality. While, the water of Youkous and source are very good quality.

3.2. Adsorption kinetics of the humic substances in the various mediums of mineralization

The aim of this essay is to determine the optimal removal yield of the humic substances on activated carbon powder in media of variable mineralization. The results (Fig. 4) show firstly that the yields of elimination of the humic substances increase in the mineralized waters with increasing stirring time of aqueous solutions and reach values ranging from 92.10% to 100%. On the other hand, the equilibrium is reached in a time interval ranging from 30 to 240 min. Table 1 recapitulates the results obtained.

Through our results, we can say that the reaction rate is quick in the case of drilling water of Biskra and the tap water, which are characterized by a very high mineralization in comparison with the water of Youkous and the source weakly mineralized. To better understand the adsorption phenomenon of the humic substances on activated carbon, we have made additional tests on the adsorption of humic substances on powder activated carbon in distilled water. The results we obtained are summarized in Table 2. In view of these results, we can say that despite the good removal yield of the humic substances in the distilled water, the equilibrium is reached for quite a long in comparison with those obtained in mineralized water.

One would expect that good yields are obtained with the highly mineralized water, but our results lead to an inversion in the order:

$$\text{Yields}_{\text{Source water}} > \text{Yields}_{\text{Youkous water}} > \text{Yields}_{\text{Drilling water}} > \text{Yields}_{\text{Tap water}}$$

We refer to the work of Yahiaoui [8] and Amimeur et al. [9], this effect may be due to the presence in the water of tap and drilling a high mineralization accompanied by a high concentration of chlorides and sulfates. Therefore, the mineralization has a notable influence on the removal efficiency of humic substances, either globally or through specific minerals. Similarly, the strong adsorption of humic substances on powder activated carbon is probably due to the pore size of the fact that the powder activated carbon is mesoporous [10]. We will be able to say that the origin and nature of humic materials, grain size and pore size distribution of the adsorbents as well as the physicochemical characteristics of the

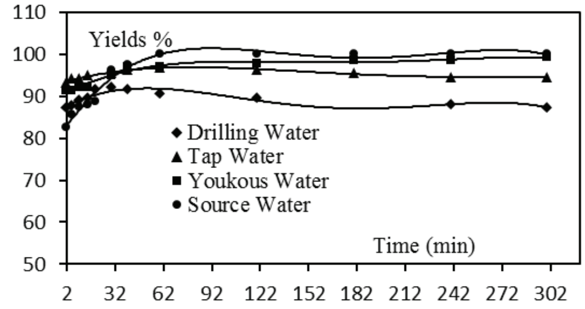

Fig. 4. Adsorption kinetics of the humic substances on the mineralized water. [HS] = 10 mg/L; [PAC] = 1 g/L; pH = 7 ± 0.1.

Table 1
Maximum yields (*R*) of removing humic substance in media of variable mineralization and equilibrium time [HS] = 10 mg/L; [PAC] = 1 g/L; pH = 7 ± 0.1

Mediums of dilutions	Yields (*R*) %	Equilibrium time (min)
Drilling water	92.10	30
Tap water	96.40	40
Youkous water	98.57	60
Source water	100	240

Table 2
Maximum yields (*R*) of removing humic substance in distilled water [HS] = 10 mg/L; [PAC] = 1 g/L; pH = 7 ± 0.1

R %	Equilibrium time (min)
92	300

medium affect significantly the removal efficiency of humic substances. Similarly, Blacke et al. [11] have shown that the adsorption of organic compounds such as humic substances would depend not only on their affinity with respect to the adsorbent, but also on interaction with the solvent itself.

3.3. Effect of the variation of the mass of adsorbent on the elimination of humic substances in the various mediums of mineralization

The results obtained in the equilibrium are presented in curves of Fig. 5. They show that the removal of humic substances varies with the mass of adsorbent involved. We also registered that good removal efficiencies of humic substances are obtained for high masses of adsorbents. Based on the results obtained, it allowed us to assume that the matrix mineral water tested can play an important role in the tests of adsorption. The presence of important quantities of inorganic compounds promoters such as calcium, magnesium, and other may explain significantly the retention of organic matter like the humic substances.

Our results can be correlated to the work of different researchers [8–10], they recorded that there is an increase in the removal efficiency of organic matter regardless of (irrespective) their nature (humic and non-humic) when the mass of adsorbent introduced increases. This increase could be up to 1,000 mg of PAC for the removal 87.60% of humic substances.

3.4. Effect of the variation of the initial content of humic substances on the elimination of humic substances by adsorption in the various mediums of mineralization

The analysis of these results (Fig. 6) indicates that humic substances are strongly retained on 1 g of PAC, although yields undergoing a reduction with increasing content of humic substances. However, these yields always stay above 50%. Thus, a desorption phenomenon appeared for the high masses of the adsorbent material. This phenomenon can be explained according to Li et al. [12] by electrostatic repulsion forces that are taking place between the organic molecules, not only between those retained to the surface of the activated carbon and the adsorbed molecules. But also, those between surface adsorbed and those in solutions. They also indicated that neutral pH (as the reaction medium in our tests); the humic compounds are ionized and carry negative charges. Therefore, when the concentration of organic material is important this promotes repulsive interactions between the molecules.

It is interesting to annotate that the exploitation of our results under the laws adsorption of Freundlich and Langmuir by considering a fixed adsorbent concentration (1,000 mg/L) and doses varying of humic substances (2–12 mg/L). Remembered that these laws are expressed in the following sections.

3.4.1. Freundlich law

$$q = \frac{x}{m} = k \cdot C_e^{1/n}$$

where k and n are constants characteristic of the effectiveness of a given adsorbent given with solute; q is the maximum adsorption capacity per unit of mass of adsorbent (mg/g) and C_e is the concentration of the substance remained in solution at equilibrium.

3.4.2. Langmuir law

$$q = x/m = q_m.\ bC_e/1 + bC_e$$

where q_m is the maximum adsorption capacity (mg/g) and b is the constant related to the adsorption equilibrium.

The exploitation of the equations of Langmuir and Freundlich enable to calculate the adsorption parameters which are summarized in Tables 3 and 4.

These results showed that the constants of Freundlich and Langmuir as well as the coefficients of linear adjustments are consistent with the results of removal efficiency of humic substances and the correlation coefficient close to 1. This indicates that the models of Freundlich and Langmuir suitable to describe the fixing of humic substances whatever the nature of water mediums tested. The retention of humic substances obeys to an adsorption phenomenon. The maximum capacity adsorption q_m is in accordance with the overall change in removal efficiency of humic substances.

The characteristic constants (k, n) join the Freundlich equation results obtained by Ayele et al. [2], Leclerc [10] and Khirani [13].

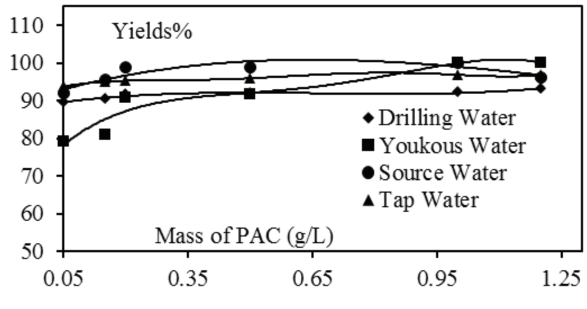

Fig. 5. Effect of the variation of the mass of adsorbent on the elimination of humic substances (HS) in the various mediums of mineralization. [HS] = 10 mg/L; pH = 7 ± 0.1.

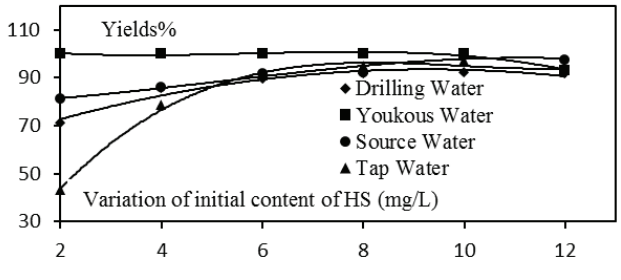

Fig. 6. Effect of the variation of the initial content of humic substances, on the elimination of humic substances by adsorption on powder activated carbon in the various mediums of mineralization. [PAC] = 1 g/L; pH = 7 ± 0.1.

Table 3
Adsorption constant of Freundlich model

Medium of dilution	*N*	*k*	*r* (%)
Drilling water	6.85	1.16	94
Tap water	8.06	2.75	95
Youkous water	50	1.22	94
Source water	0.88	46.56	99

r %: Correlation coefficient.

Table 4
Adsorption constant of Langmuir model

Medium of dilution	q_m (mg/g)	*b* (mg^{-1})	*r* (%)
Drilling water	0.94	0.75	94
Tap water	2.27	0.38	99.6
Youkous water	0.25	2.67	96
Source water	0.60	0.015	93

4. Conclusion

Our study was part of the overall framework of the search for improved treatment of water intended for human consumption. We also insisted on the presence of humic substances. Because, they are usually the most important category of surface water.

At very high concentrations, these substances can procure to the water a yellowish or brownish color and unpleasant taste or odor. These macromolecules with complex structures seem difficult to remove in the absence of certain optimal conditions during conventional treatments.

It is interesting to note that our objective was to test the performance of PAC in the removal of humic substances in mediums of variable mineralization.

According to the physicochemical characteristics of the water tested. Our results have been well registered that the water from the regions of southeastern regions of Algeria are of poor quality, requires treatment thrust before they are distributed to consumers. While the water come from the eastern Algeria are of very good quality.

Similarly, our results have well proven that the adsorption can make an important contribution to the elimination of matter organic type humic. Moreover, that the mineral composition of the water tested has played an important role in the adsorption mechanisms. The presence of large quantities of inorganic compounds promoters or inhibitors may explain the differences observed and make the retention of matter organic type humic meaningful. The Freundlich and Langmuir isotherms appeared the effectiveness of PAC and the increase of the adsorption capacity clearly through the exploitation of our results.

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