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Valorization of the common reed in the adsorption of silver nitrates

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***ABSTRACT** : the goal of this study is the clarification of an activated carbon containing the common reed (reeds australis) in order to use it as adsorbent of pollutant, then to compare its results of adsorption with those of the commercial activated carbon. the transformation of the reed into activated carbon is obtained by thermochemical way by using phosphoric acid like agent of activation. the tests of adsorption were carried out on silver nitrates, with variation of two parameters namely the initial concentration of this last and it time of agitation. the results of adsorption got for two coals under the same operating conditions are very satisfactory; that se perceives through the maximum outputs which are about 72% for the activated carbon resulting from the common reed and about 68% for the commercial activated carbon. the results of adsorption were exploit using the models of langmuir and freundlich. the common reed has the advantage of being at the same time inexpensive and very effective in the field of water treatment.*

***KEYWords :** adsorption, activated carbon, common reed, pollutant, water treatment.*

I. INTRODUCTION

The world interest carried to the safeguarding of the environment of the solid waste induced by the various activities and human transformations, caused the attention of the researchers to find average the techniques to develop this waste [1]. The removal of pollutants in aqueous solutions by adsorption on different solid materials, in particular on activated carbon, has been the subject of much work [2-3].

The development of research on active carbons in Africa is part of the use of biomass to produce new materials, and enables scientifically accompany the processes of pollution and industrial development [4].

The development of the activated carbon starting from the vegetation wastes is interesting from an economic standpoint because it is starting from simple transformations that a direct application of these materials is carried out [5]. Among the latter our choice it is related to the common reed (Reeds australis) for the adsorption of silver nitrates ($AgNO_3$). Its use as adsorbent is due to its abundance in nature since it is a species colonizing and invading with rapid growth [6].

II. Objective

The objective of this work is the elimination of silver nitrate ($AgNO_3$) in an aqueous medium with a less expensive adsorbent; made from common reed of Kabylia region of Algeria.

The first step of this study is oriented towards the development of our adsorbent and preparation of synthetic solutions. Secondly, we proceed by the elimination kinetics of the silver nitrate to determine the maximum amount adsorbed and present the adsorption isotherms. We conclude this work by a comparative study of the adsorption capacity of our activated carbon developed with that of commercial activated carbon. It should be noted that adsorption takes place under the influence of environmental temperature (ambient), the stirring speed (150 rev / min), medium pH (neutral) and porosity of the adsorbent.

III. MATERIELS AND METHODS

A. *Protocol of manufacturing of the activated carbon starting from the common reed*

The activated carbon was prepared according to the experimental protocol developed by BADI [7]:

The reed is cut out in several small pieces, then crushed until obtaining a powder which is preserved safe from the air in hermetically closed bottles then one proceeded has the impregnation with the phosphoric acid, into each beaker one introduced 50 G of the broyat with 200 ml of the solution of H_3PO_4 (50%). Once finished the mixture is left safe from the light during 24:00.

1. The pasty mixture is versed in ceramics containers, put in the oven at pulley block (standard LM 512.07) at a temperature of 150°C during 1:00, and then increased with 300°C for one hour moreover, then with 450°C during four hours.

2. After cooling of the mixture, one washes it several times, with distilled water heated to eliminate all the residual acid, until a neutral pH (pH= 7), then it is filtered. The filtrate obtained is dried in a drying oven with 105° C during 24:00, to its exit of the drying oven one passes it through a sieve of 50µm. Coal manufactured is ready with the use.

B. Preparation of the solutions

In parallel one prepared several silver nitrate solutions ($AgNO_3$) of various concentrations going of 0.01 mol/l until 0,1mol/l with a step of 0.01 mol/l. For each silver nitrate concentration, we add 1g of elaborate activated carbon, after agitation we passe to the spectrophotometric analysis using a spectrophotometer of the type biochrom Libra S6. The same stages are made with commercial coal to be able to make a comparison.

Our study is conducted at room temperature (26 ° c), The elevation of the temperature disadvantaged the adsorption phenomenon [8]. The best results are obtained in the field of the room temperature [9].

C. Electron microscope with sweeping (MEB)

The scanning electron microscope is a scientific instrument to create images of the surface of 3D objects with a very high resolution of a nanometer (billionth of a meter). The resolution of a magnification instrument is defined as the minimum detectable size by the human eye on the image produced by this instrument. This means that an image produced by a SEM allows to distinctly differentiate two points separated by less than one nanometer. it possible to obtain images of surfaces of practically all solid materials, on scales going from that of the magnifying glass (x10) to that of the electron microscope in transmission (x500.000 or more). These images strike in first by returned very speaking about the relief and the great depth about field [10].

For this study we used an electron microscope with sweeping (MEB) of brand PHILIPS ESEM XL 30 and the tensions of acceleration of the electronic beam were of 20 Kv, for a distance from penetration of 100 µm.

VI. RESULTS AND DISCUSSIONS

a- *Result of SEM*

Analysis at the scanning electron microscope has allowed us to compare the morphology of the coal from the common reed before and after activation (Fig.1).

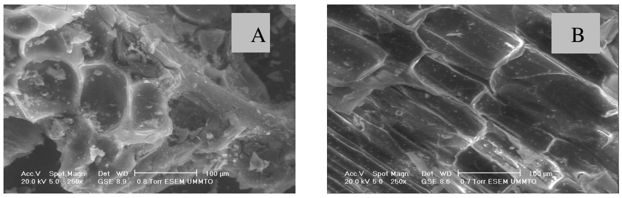


Fig.1. Common Reed to the SEM:
A- before activation, B- after activation

The images show that the coal produced by the common reed has a highly developed porosity with some heterogeneity. The porosity is related to the distribution of the pore size. It reflects the internal structure of the microporous adsorbents [11]. This can be explained by the fact that activation at increasing temperatures allows an increase in surface area, while increasing its porosity [12]. The adsorption is proportional to the specific surface of the adsorbent [13].

b- *Kinetic of adsorption of silver nitrate on the common reed and commercial coal*

The adsorption at the interface solute / solid is a phenomenon of physical or chemical nature whereby the molecules present in liquid or gaseous effluent, attach to the surface of a solid [14]. This phenomenon depends both on this interface and the physicochemical properties of the adsorbate [15].

Also the texture of the activated carbon is essentially characterized by two parameters which are the surface area and porosity. They are essential for the determination of capacity and adsorption kinetics [16]

The adsorption isotherms of silver nitrate on the common reed and commercial coal are shown in Fig2.

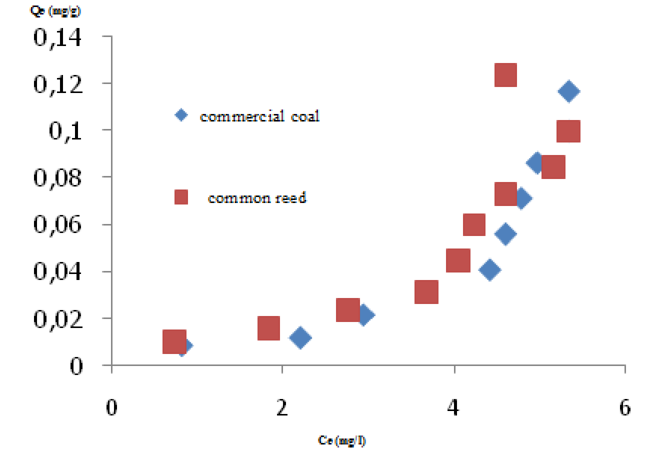


Fig.2. Adsorption isotherm of silver nitrate on the common reed and commercial coal

The curves given in Fig 2, indicate that the equilibrium concentration of silver nitrate increases with the increase of the amount adsorbed, confirming the influence of the concentration on the amount of adsorbed silver nitrate.

For an equilibrium concentration of 5.338 mg / l, the maximum amount adsorbed is 0.0995 mg / g for the reed and 0.116 mg / g for commercial coal.

C- Modeling of adsorption kinetics

All systems adsorbent / adsorbate do not behave the same way. The adsorption phenomena are often addressed by their isothermal behavior. The isothermal curves describe the relation existing at adsorption equilibrium between the adsorbed amount and the solute concentration in a given solvent at a constant temperature.

- The solvent is adsorbed on the same sites as the solute. This implies the existence of an adsorption competition between solvent and solute.

-The attractive or repulsive interactions between the adsorbed molecules are manifested in a significantly in the adsorption phenomenon.

- The number of suitable sites for the solute molecules to the solid surface decreases when the amount adsorbed increases. **[17]**

Traditional models of Langmuir and Freundlich characterizing the formation of a monolayer will be used for their simplicity of implementation [18] and [19].

- *Model of Langmuir*

$$q = \frac{q_m K_a C}{1 + K_a C}$$

With :

q: Quantity of silver nitrate adsorbed by the carbon;

qm: maximum adsorption quantity;

C: Concentration in solution at adsorption equilibrium;

Ka: constant of specific adsorption of the adsorbate on coal.

Linearization of the Langmuir relationship gives the following equation:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{K_a q_m C}$$

- *Model of Freundlich*

The Freundlich equation is well suited to describe the equilibrium in aqueous phase [20].

$$q_e = K_F C_e^{\frac{1}{n}}$$

qe: Quantity adsorbed per gram of solid;

Ce: concentration of the adsorbate in the adsorption equilibrium;

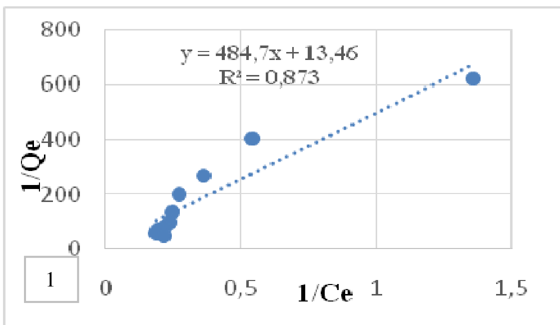
Kf and n: are constants of Freundlich, indicative of the intensity and the adsorption capacity [20].

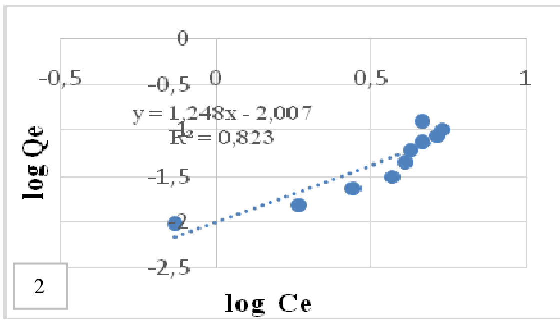
The linear form is given by the following equation:

$$\log Qe = \log k + \left(\frac{1}{n}\right) \log C_{eq}$$

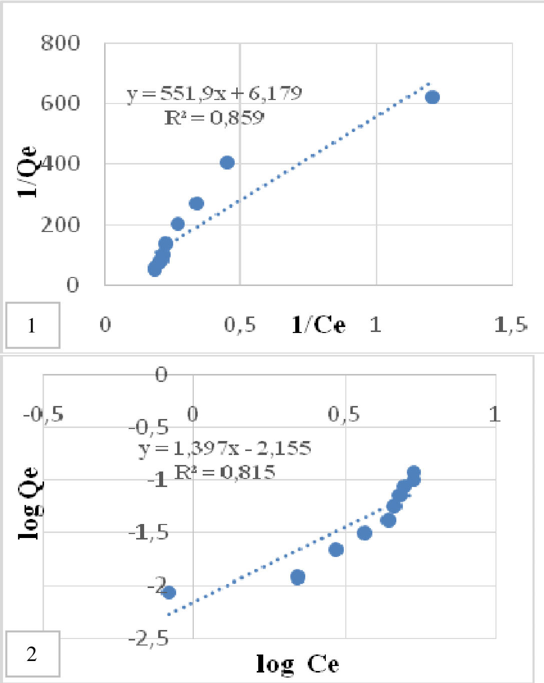
The slope of 1 / n between 0 and 1 is a measure of the absorption intensity or surface heterogeneity, becoming more heterogeneous than its value approaches zero [21].

The linear forms of the Langmuir model and Freundlich are shown in Fig .3.





common reed



commercial coal

Fig.3. Adsorption of silver nitrate according to the isotherms of:
(1) -Langmuir and (2) - Freundlich

The modeling of the experimental results produced charcoal and trade coal thereby than the maximum adsorption amounts are given in Table (I). The Comparison of correlation coefficients obtained with both models for both coals show a better agreement with the Langmuir model.

Table I
Parameters of adsorption models of silver nitrate

The adsorbents used	Langmuir			Freundlich		
	q_m	K_a	R^2	K_f	n	R^2
common reed	*0,074*	*0,0278*	*0,873*	*0,711*	*0,801*	*0,823*
commercial coal	*0,162*	*0,0112*	*0,859*	*0,563*	*0,716*	*0,815*

We note that the correlation coefficients (R2) are obtained for both models close to unity, which explains the concordance of experimental results with these models.

The adsorption of silver nitrate follows the Langmuir model with maximum adsorption amount of 0.074 mg / g for the common reed and 0.162 mg / g for commercial coal.

The value of the heterogeneity factor (n) of Freundlich is less than unity, the silver nitrate are favorably adsorbed by the reed.

a- Influence of the concentration of silver nitrate and stirring time on yields

• *Influence of the initial concentration on yields*

According to the results, we note that the adsorption performance of silver nitrate on the reed are slightly higher than those of the commercial coal with maximum retention of 72.90% for an initial concentration of 16.987 mg / l, and 68.58% in the commercial coal for the same initial concentration.

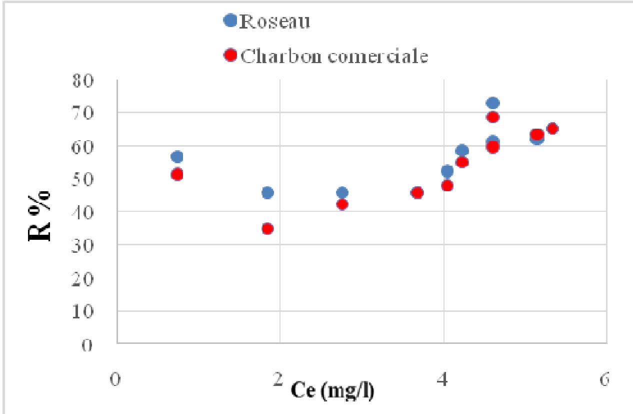


Fig. 4. Influence of the concentration of Silver Nitrate on yields.

- *Influence of the contact time*

The contact time is a very important parameter in an adsorption process [22]

Before its adsorption, the solute will pass through many stages [23]

1) - Diffusion of the adsorbate of the external liquid phase to that in the vicinity of the surface of the adsorbent.
2) - Diffusion of the extragranular material (transfer of solute through the liquid film to the surface of the grains).
3) - Transfer intragranular of the material (transfer material into the porous structure of the outer surface of the seeds to the active sites).
4) - Reaction of Adsorption with active sites, once adsorbed, the molecule is considered motionless.

We have an adsorption which is carried out in two parts; the first part is a rapid adsorption after 20 minutes for both studied coals; this phase corresponds to a transfer of silver nitrate from the liquid phase on the surface of activated carbon. This phenomenon observed during the first minutes of adsorption, can be interpreted by the fact that at the beginning of the adsorption the number of active sites available on the surface of the adsorbent material is much more important than that of the remaining sites after a certain time [24]. The adsorbed molecule is attached to a specific site and can freely move to the interface. Physisorption is rapid, reversible and does not result in changes of the adsorbed molecules [25].

The second part is slower, this area is the establishment of a balance between the rates of adsorption and desorption rate of our activated carbon

I. CONCLUSION

The use of natural inorganic materials as adsorbents became a field of research most as referred to many researchers. Although, the adsorbents used can vary due to the variation of the adsorption conditions; according to the type and number of pollutants, and properties that affect the efficiency of an adsorbent such as specific surface area, the size and the pore homogeneity, structural properties, the selective adsorption capability and ease of regeneration [26]. Also the high cost limits the use of activated carbon who encourages us to seek more affordable alternative materials and a comparable efficiency.

The experimental tests we have carried out, have been devoted to the elimination of silver nitrate by adsorption on activated carbon in powder from the common reed.

The experimental results have been adapted by a kinetic study indicating that the adsorption follows the first order kinetics and thus by a modelization by the models of Langmuir and Freundlich isotherm where the Langmuir model is more descriptive of the studied adsorption. And the results have been found successful in satisfactory yields.

After comparison, the adsorption performance on the reed is more important compared to that of the commercial coal and is in the order of 72% and 68% respectively.

The study that we carried out showed that the activated carbon from the common reed has a considerable capacity of adsorption and is approaching very clearly from that of commercial coal with similar affinities.

This work can be subject to further study in order to a large-scale marketing of this natural adsorbent of plant origin and inexpensive.

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