



Preparation and characterization of new adsorbents of pea and bean agricultural peels for water purification loaded with organic tryptophan compound

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ABSTRACT

The aim of the study was to find alternative materials that could contribute to the protection of the environment by the elimination of organic pollutant (tryptophan). The adsorbent materials (activated carbon) were prepared from pea and bean peels which were chemically treated with phosphoric acid and then treated physically by calcination. This synthesized material was used as an adsorbent for the purification of different waters charged with organic tryptophan compound. Agricultural residues were characterized by electronic microscopy and thermogravimetric analysis. The physical characterization was determined by adsorption of nitrogen gas at 77 K (BET). The impact of some process parameters was examined and analyzed, namely the initial concentration of pollutant, the dose of activated carbon and the dilution medium. The obtained results showed a low yield between 10% and 33% in the three types of water for coagulation–flocculation with aluminum sulfate alone. However, better removal efficiency was obtained by combination of aluminum sulfate and activated carbon between 70% to 90%, and elimination efficiency between 75% to 80% in combination with aluminum sulfate and activated carbon. Specific areas of pea and bean peels respectively 735.27, 760.56 m²/g, and the diameter of its pores respectively 58.42 and 52.88, make these adsorbent materials efficient, economical and effective for the removal of organic matter.

Keywords: Pea peels; Bean peels; Coagulation; Adsorption; Tryptophan

1. Introduction

Current water needs are only met by the use of other water sources, such as surface water, seawater and brackish water, which are more or less polluted and salty.

The use of polluted water is very dangerous and disrupts the aquatic ecosystem. Natural organic matter is present in all natural waters. It is a complex heterogeneous mixture of various organic compounds which varies according to

the molecular size, structure, and chemical composition. This organic matter plays a very important role in determining the quality of the water and its treatment.

There are several physical, chemical and biological methods to treat and decolorize polluted effluents such as coagulation and flocculation, biodegradation, membrane filtration, chemical oxidation, ozonation, ion exchange, electrochemical methods, photocatalytic technics, adsorption, etc. [1,2].

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Flocculation/coagulation is a physico-chemical process for water clarification. Its main role is to remove the non-settling matter that is present in the water in colloidal form.

Coagulation represents the whole of physical and chemical phenomena aimed at destabilizing a solution of very small particles of negative charge, called colloids (diameter $<1 \mu\text{m}$), and promoting their agglomeration.

Selective and non-selective adsorption is another removal process that has been the subject of several studies and has been widely applied in the removal of various pollutants.

Currently, the lookout for better-performing and more innovative materials is the main goal of researchers around the world [3–5]. The biomaterials from agricultural wastes such as lemon peel [6,7], coffee grounds [8], apple peel [9], date cores [10] and apricot cores [11], with a high percentage of carbon can be used as precursors for the production of activated carbon. These precursors are cheaper and renewable compared to industrial activated carbon [12–14]. Agriculture residues are the most used basic materials in the preparation of activated carbon.

Many authors have studied the preparation of activated carbon from different raw materials for use as effective adsorbents against pollutants that are likely to be present in aqueous media [14,15]. Unfortunately, all of these materials are expensive. This encouraged the use of adsorbents, which appear to be cheaper, easier and more effective [16–18].

Lignocellulosic materials are mainly generated in agricultural activities. Therefore, they are sometimes referred to as agricultural wastes or residues. These wastes arise from different parts of plant materials, such as stems, leaves, roots, fruit peels, which are mainly composed of cellulose, hemicellulose and lignin. Lignocellulosic materials have strong ion attraction forces due to their high content in hydroxyl groups [19].

Hence, the overall goal of this study was to examine the removal of organic pollutants. In this aim, the elimination of tryptophan, in different types of water (distilled water, dam water and seawater), was examined by coagulation–flocculation/adsorption with commercial activated carbon (CAC), pea peels activated carbon (CAPP) and bean peels activated carbon (CAPB) prepared from agricultural wastes.

2. Materials and methods

2.1. Raw materials

Raw materials came from agricultural products. They are pea skins (PP) or bean skins (PB). These vegetables were collected in the region of Sétif, north-central Algeria.

CAC used during our experiments was in powder form; and it is a product of the company Riedel-de Haën (France).

2.1.1. Adsorbents

After separating the pea and bean from the peels, we dried the peelings by exposing them to sunlight for several days to remove the moisture from the peels. Afterwards, the pea peels (PP) and the bean peels (PB) were crushed and sieved to obtain a homogeneous powder. Then (PP, PB) were washed several times with hot distilled water, to remove impurities, until the rinsing liquid was clarified. After this step, the material was dried at 60°C for 48 h

and then ground a second time to obtain a powder with homogeneous granules.

2.1.2. Preparation of activated carbons

In literature, there are several methods of preparing activated carbons, both physical and chemical. The preparation of activated carbons from agricultural residues using the chemical activation method has been the subject of many studies [20,21]. The main objective of this study is to prepare activated carbons from pea peels (CAPP) and CAPB in order to obtain a product applicable in water treatment. The used activating agent was phosphoric acid (H_3PO_4), which has been widely utilized for the activation of carbons among the available acids [22,23]. For this purpose, 10 g of each raw sample were mixed with a solution H_3PO_4 of concentration of 1.5 mol/L for pea peels (PP) and a concentration of 3 mol/L for bean peels (PB) kept stirred (250 rpm) for 10 h. The mixtures were then placed in an oven for 24 h at 110°C .

The products were placed in a calcination furnace, with a heating rate of $10^\circ\text{C}/\text{min}$ and kept at a temperature of 450°C for 1 h. The products obtained after calcination, CAPP and CAPB were washed with a sodium hydroxide solution (1 mol/L), and then were washed with distilled water several times up to $\text{pH} \approx 6.5$. The products were then dried at 110°C for 24 h [24].

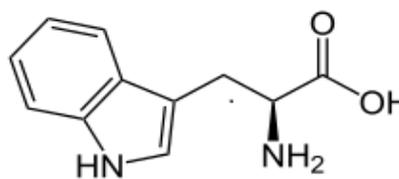
2.2. Coagulant

Aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) powder, with a molar mass equal to 666.65 g/mol, was used as the coagulant reagent; it was prepared by dissolution in distilled water. A stock solution of 10 g/L was prepared periodically.

2.3. Solutions of the organic compound

The tested organic compound was tryptophan (amine acid) which contains carboxylic function in its chemical structure (Table 1). Tryptophan was purchased from Aldrich. The synthetic solutions of tryptophan ($C_0 = 100 \text{ mg/L}$) were

Table 1
Characteristics of the organic acid tested [25]

Chemical structure	
Symbol	Try
pKa $-\text{COOH}$	2.4
pKa $-\text{NH}_3^+$	9.4
Isoelectric point	5.89
Solubility (g/100 g) of water	1.136
Chemical formula	$\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2$
Molar mass	204.22 g/mol
Fusion point	290.5°C

prepared by dissolving in three types of water: distilled water, water withdrawn from Kherrata dam and seawater.

2.4. Dilution media

2.4.1. Distilled water

The distilled water used in the present study had a conductivity varying between 2 and 5 $\mu\text{S}/\text{cm}$ and a pH close to neutral, varying from 6.45 to 6.66.

2.4.2. Surface water

The experiments were carried out on the raw water of the Kherrata dam, located around 60 km from Béjaia, bordered to Sétif.

2.4.3. Seawater

Seawater was characterized by its concentrations of dissolved salts, which varied from 33.000 to 37.000 mg/L. The seawater used in the different tests came from Lotta beach, which is located in Béjaia.

Some physico-chemical characteristics of the dam water and seawater are presented in Table 2.

2.5. Specific surface area (m^2/g) BET

The specific surface area was measured by the BET procedure using a Micromeritics ASAP 2020 apparatus. The samples were weighed and degassed under an inert atmosphere for 6 h and at a temperature not exceeding the synthesis temperature. The degassing was carried out at 77 K for 20 h. The specific surface expressed in m^2/g is given by the following relation:

$$S_{\text{BET}} = \frac{(V_m \cdot N_A \cdot a_m)}{(V_M \cdot m)} \quad (1)$$

where S_{BET} : specific surface area obtained by the BET method ($\text{m}^2 \text{g}^{-1}$ of adsorbate); a_m : surface area occupied by the N_2 molecule (0.1627 nm^2); V_m : volume of the monolayer (cm^3/g); V_M : molar volume of the adsorbate N_2 ($22,414 \text{ L/mol}$ at TPN); N_A : Avogadro number ($6.023 \times 10^{23} \text{ mol}^{-1}$); m : mass of the sample (g).

2.6. Determination of the moisture content

The moisture content is a ratio that is expressed as a percentage; it is determined by drying the adsorbent in an oven [21]. A sample of 0.5 g for each of the following samples, PP, CAPP, PB, CAPB and CAC, was placed in a ceramic crucible and then weighed. Afterwards, it was dried in an oven at 110°C until its weight remained constant. Once removed from the oven, the sample was cooled to room temperature and reweighed.

The moisture content (% H) can be calculated by the following equation:

$$\%H = \frac{(M_{H3} - M_{H2})}{M_{H1}} \times 100 \quad (2)$$

Table 2

Physico-chemical properties of dam water and seawater

Parameters	Kherrata dam	Seawater
Temperature ($^\circ\text{C}$)	21.9	18
pH	7.45	9.75
Conductivity ($\mu\text{S}/\text{cm}$)	1.074	54
Turbidity (NTU)	2.3	2.95
UV absorbance at 254 nm	0.01746	0.003
TDS (g/L)	531	29.4
Ca^{++} (mg/L)	101.6	414
Mg^{++} (mg/L)	35.48	1,396.56
Na^{++} (mg/L)	58.1	10,125
K^+ (mg/L)	2.9	435
SO_4^{2-} (mg/L)	265	2,773
Cl^- (mg/L)	95.85	18,234.6
HCO_3^- (mg/L)	244	161.04
NH_4^+ (mg/L)	0.17	<0.02
NO_2^- (mg/L)	0.09	<0.02
PO_4^{2-} (mg/L)	0.0	<0.09

TDS, Total dissolved solids.

where M_{H1} : initial mass of PP, CAPP, PB, CAPB and CAC used (g); M_{H2} : mass of the filled crucible after drying (g); M_{H3} : mass of the filled crucible before drying (g).

2.7. Determination of the ash content

0.5 g sample of PP, CAPP, PB, CAPB, CAC was dried in an oven at 80°C for 24 h and then placed in a ceramic crucible. This crucible was introduced into an oven set at 650°C and kept for 3 h at this temperature. After cooling to room temperature, the crucible was again weighed [21].

The ash content (% C) was calculated as follows:

$$\%C = \frac{(M_{C3} - M_{C2})}{M_{C1}} \times 100 \quad (3)$$

where M_{C1} : initial weight of PP, CAPP, PB, CAPB and CAC used (g); M_{C2} : weight of the crucible before carbonization (g); M_{C3} : weight of the filled crucible after carbonization in (g).

2.8. Coagulation–flocculation tests

The Jar tests were carried out on an agitator plate. Solutions, enriched with the model pollutant and the coagulant, were subjected to a rapid agitation of 200 rpm for 3 min. The speed was then reduced to 60 rpm for 30 min. After a settling time of 30 min, the pollutant removal yield was determined.

These experimental conditions that were applied in our tests, which correspond to the time, the agitation speed and the settling time applied in the fast and slow phase can be justified by the results of previous studies [26] related to the coagulation–flocculation of various organic compounds.

The percentage of elimination was determined by the yield that is expressed by:

$$\%R = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (4)$$

where C_0 and C_f represent the initial and final organic compound concentrations expressed in mg/L.

2.9. Coagulation/adsorption tests

The combined coagulation/adsorption tests in distilled water, surface water or seawater were carried out with aluminium sulfate (SA) and carbon activated commercial powdered (CAC), CAPP or CAPB. The tests were carried out taking into account different parameters: dose of activated carbon, optimal dose of coagulant and initial concentration of organic compound.

3. Results and discussions

3.1. Specific surface area BET

The results of the adsorption–desorption isotherms of activated carbons are shown in Table 3. The table presents the different parameters of texture, namely the nature of the various considered samples, the BET surface area

(S_{BET} m²/g), the external surface area (S_{ext} m²/g), the microporous surface (S_{mic} m²/g), the total pore volume (V_{TP} cm³/g), the microporous volume (V_{mic} cm³/g), the mesoporous volume (V_{mes} cm³/g) and the average pore diameter.

According to Table 3, it can be seen that the BET surfaces of activated carbons were higher than those of the raw materials. This can be attributed to the chemical treatment which has a great effect on the textural properties of the adsorbents, and the adsorption properties of the carbons depend mainly on their surface chemistry (specific surface area, pore size, etc.) [27].

After the activation of PP and PB by H₃PO₄, their specific surface areas increased significantly, from 1.17 to 735.27 m²/g for PP and from 0.85 to 760.56 m²/g for PB. The specific surface area of CAC was 721.3 m²/g. The microporous volume of activated carbon CAPP was the largest compared to CAPB and CAC. By comparing the pore diameters, it can be noted that CAC (71.96 Å) > CAPP (58.42 Å) > CAPB (52.88 Å), showing that the CAC displayed the highest adsorption capacity.

The pore size distribution showed therefore that the surfaces of carbons activated with H₃PO₄ were mostly microporous and can be promising adsorbents for large organic molecules.

Adsorption/desorption isotherms of nitrogen at 77 K for commercial and activated carbons prepared from pea and bean peels residues are summarised in Fig. 1. It can be seen

Table 3
Textural properties obtained from N₂ adsorption/desorption studies on the various samples, PP, CAPP, PB, CAPB, CAC

Type	S_{BET} (m ² /g)	S_{ext} (m ² /g)	S_{mic} (m ² /g)	V_{TP} (cm ³ /g)	V_{mic} (cm ³ /g)	Diameter pores (Å)
PP	1.17	0.83	0.36	–	–	220.15
CAPP	735.27	108.86	626.42	0.391	0.294	58.42
PB	0.85	0.63	0.22	–	–	197.34
CAPB	760.56	272.5	488.1	0.46	0.23	52.88
CAC	721.3	230.9	490.4	0.53	0.23	71.96

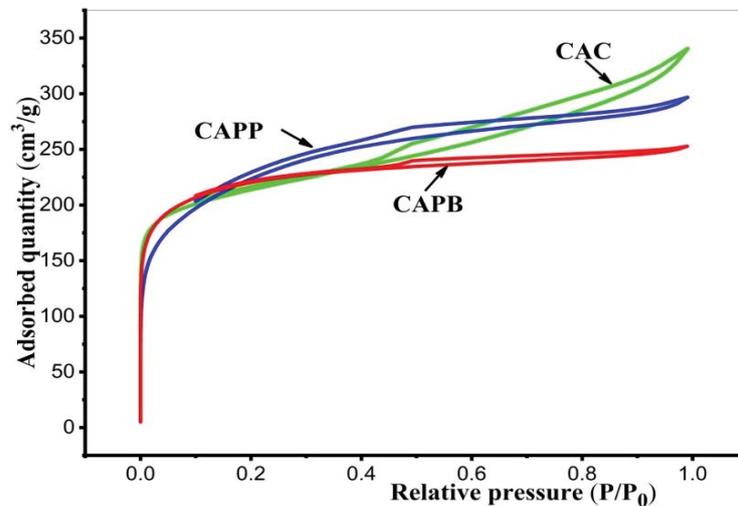


Fig. 1. Adsorption–desorption isotherms of N₂ at 77 K of commercial activated carbon (CAC), bean peel activated carbon (CAPB) and pea peel activated carbon (CAPP).

that the isotherms are of type IV of the BDDT classification (Brunauer, Deming, Deming and Teller), often observed with microporous adsorbents having more or less rigidly bound sheets between which capillary condensation can occur. The characteristic of the IV isotherms is the simultaneous presence of micropores and mesopores.

3.2. Thermogravimetry (TG)

The instrument used was a thermo-balance GA Q500. Temperature was increased from ambient up to 900°C at a rate of 5°C/min (under air). The results of the thermal analysis of the different materials are illustrated in Figs. 2–4. It can be seen that the evolution of the mass loss of PP, CAPP, PB, CAPB and CAC during heat treatment can be divided into three stages [28].

In the first stage, a mass loss of 8.5%, 7.91%, 9%, 4.39% and 4.32% was observed for PP, CAPP, PB, CAPB and CAC respectively, due to the release of water that was adsorbed below 200°C.

The second stage corresponded to the decomposition of the carboxylic groups and carbonates between 200°C and 550°C [29], leading to the loss of a large part of their mass.

The decomposition process allowed to obtain maximum mass losses when the temperature reached 305.26°C for PP with a loss of 60.1%, 527.77°C for CAPP with a loss of 56.69%, 304.6°C for PB with a loss of 53.47% and 504°C for CAPB with a loss of 73.74%.

The variation of CAC mass as a function of temperature showed a mass loss of 93.9% at 574.78°C.

The third stage corresponded to the behavior of materials (PP, CAPP, PB, CAPB, CAC) above a temperature of

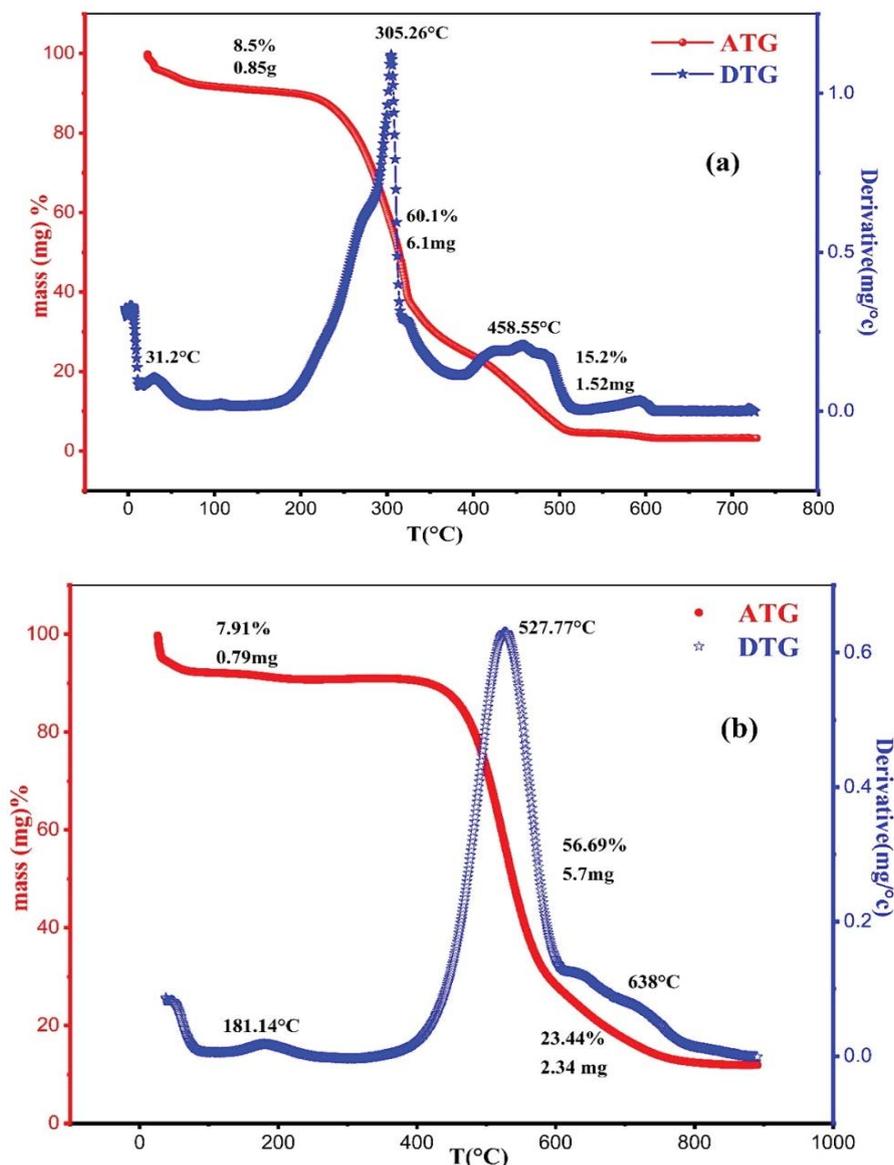


Fig. 2. Thermal analysis (ATG/DTG) for PP (a) and CAPP (b).

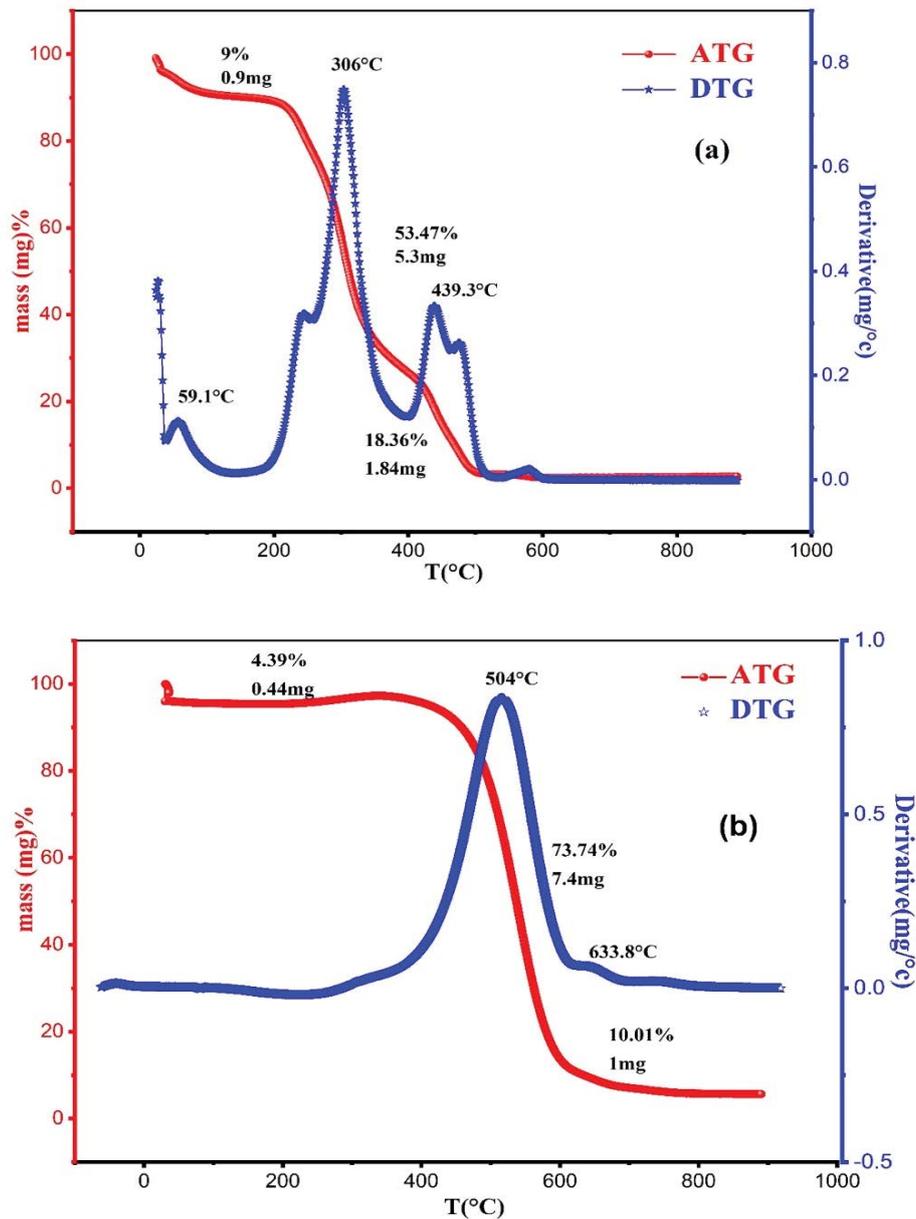


Fig. 3. Thermal analysis (ATG/DTG) for PB (a) and CAPB (b).

550°C at which they are supposed to contain inorganic substances (ash).

Maximum mass losses of 15.2% for PP, 23.44% for CAPP, 18.36% for PB, 10.01% for CAPB and 13.38% for CAC were recorded at 458.55°C, 638°C, 439.3°C, 633.8°C and 650°C, respectively.

The mechanism of the thermal decomposition of activated carbons is based on the division of the temperature into intervals. The decomposition temperature depends on the used material and the employed chemical treatment method [30], so (PP, CAPP, PB, CAPB, CAC) may contain cellulose and lignin. However, it is difficult to identify the decomposition of the particles.

As shown in Table 4, the raw materials and prepared activated carbons had a low mineral content (ash) and low

moisture content, except for the CAPP which had higher ash content (21.96%). Aside from CAPP, these results are in agreement with the results that were obtained from the literature for coconut and peanut shell, with ash contents of 0.37% and 3.71%, respectively. Low ash content indicates a good adsorbent [30].

3.3. Scanning electron microscopy

Figs. 5–9 show scanning electron microscopy (SEM) images obtained for materials PP, PB, CAPP, CAPB and CAC by a scanning electron microscopy S-2360N. From the point of view of surface chemistry and texture, different methods can be used. To characterize the surface chemistry, SEM proved that chemical activation and subsequent

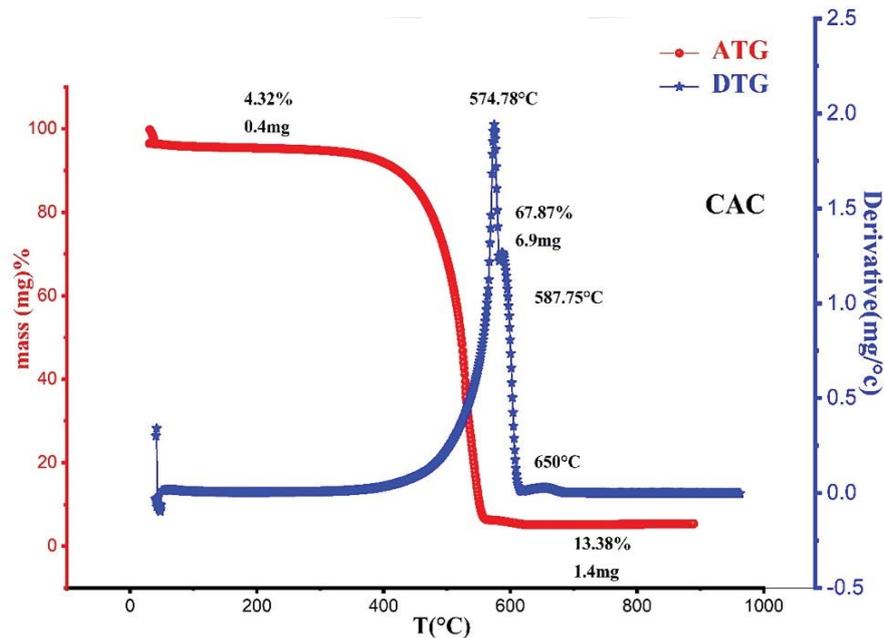


Fig. 4. Thermal analysis (ATG/DTG) for CAC.

Table 4
Moisture and ash content of PP, CAPP, PB, CAPB, CAC

Sample	Moisture (%)	Ash (%)
PP	8.5	3.8
CAPP	7.91	21.96
PB	9	6.9
CAPB	4.39	8.7
CAC	4.32	5.14

physical activation of PP and PB led to the increase in the size and opening of the pores at particle level, showing that the processes of activation and modification of agricultural residues were well carried out. H_3PO_4 can be excellent adsorbents for large organic molecules.

3.4. Coagulation experiments alone

The coagulation process is influenced by many parameters, such as coagulant composition and dose, pH, temperature, water composition, etc. The pH and coagulant dose are related parameters and this results in the influence of pH in the hydrolysis equilibria of alumina sulfate involved in the coagulation–flocculation process [31].

This section is devoted to the study of the effect of the coagulant dose and the pH on the elimination efficiency of tryptophan for different concentration values 5, 10 and 20 mg/L (Figs. 10 and 11). Solutions of volume $V = 100$ ml at temperature $T = 19^\circ\text{C}$ were subjected to rapid stirring of 200 rpm for 3 min, then to 60 rpm for half an hour and finally to a settling of 1 or 2 h.

3.4.1. Effect of the coagulant dose

By varying the dose of the coagulant in distilled water (pH = 7), dam water and seawater, the most striking fact was the appearance of two zones for the three types of water. In the first zone, the yield increase significantly up to a value corresponding to the optimal elimination of tryptophan. In a second zone, the removal yield reached a plateau even in the presence of an excess of coagulant. It was in agreement with the related literature [32,33], where it was noted that for all the concentrations tested in humic acid, there is an optimal dose of aluminum sulfate from which the yield stabilizes.

As observed, the removal of tryptophan acid was the highest in seawater by comparison with distilled water and dam water. The removal yield was the lowest in dam water, since this water already contains organic compounds apart from the tested organic compound.

The elimination efficiency of the selected organic compound increased with the increase in the dose of coagulant up to an optimal dose of 80 mg/L for all types of water. The maximum yields obtained for the concentrations ($C_0 = 5, 10$ and 20 mg/L) were (33.1%, 19.05%, 15.42%) for distilled water, (26.40%, 19.85%, 9.27%) for dam water and (27.5%, 20.14%, 18.7%) for seawater respectively. From this and as expected, the increase in concentration caused a decrease in the elimination efficiency for the three waters. The removal yields were in all cases relatively low in surface waters (dam, sea) and close to 33% in distilled water. We can also note that as the coagulant dose increases, the removal percentage becomes moderately important.

The removal efficiency of the organic matter in surface waters would be closely related to the presence of mineral and organic matrices and to their relative proportions between promoter and inhibitor elements. In our case, there

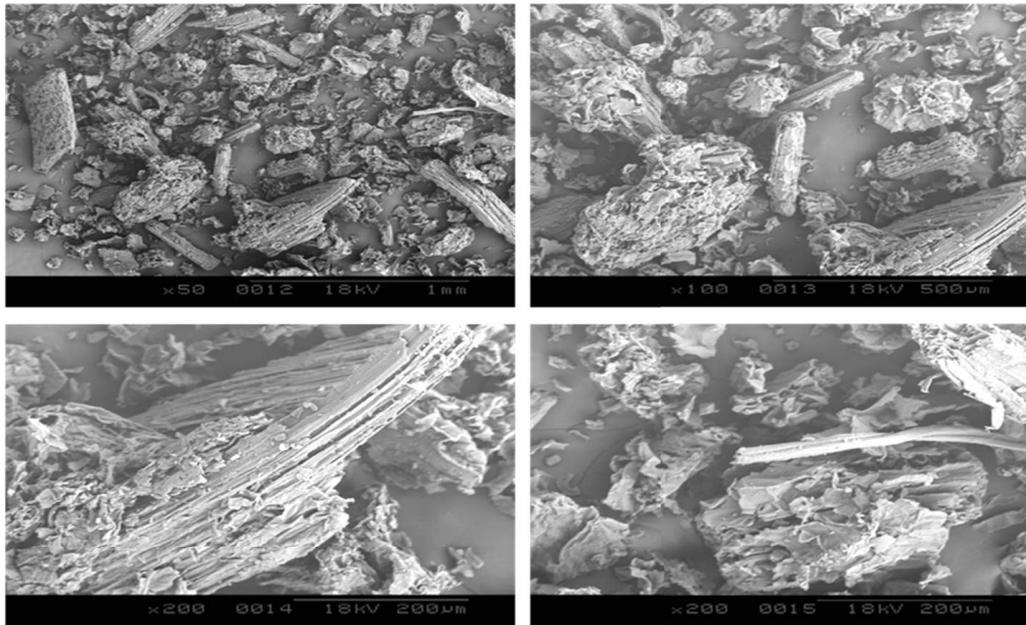


Fig. 5. SEM images of PP with 50–200 μm resolution.

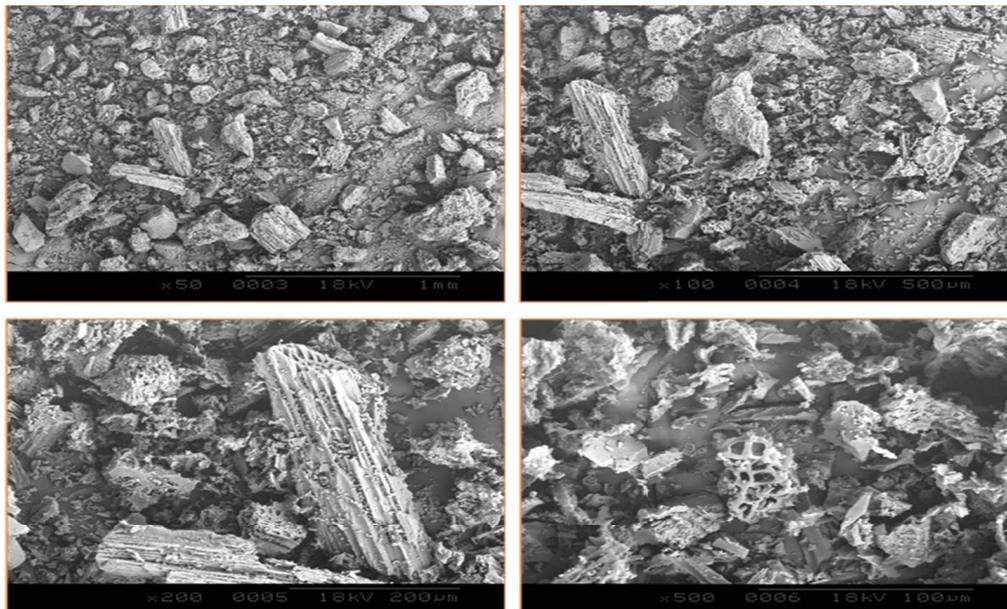


Fig. 6. SEM images of CAPP with 50–500 μm resolution.

are some mineral elements and organic compounds that have a promoting effect in the removal of tryptophan.

Excessive coagulant levels lead to destabilization of particles and increased operating costs, while inadequate dosing leads to insufficient quality of the treated water. In previous studies with pyromellitic acid, a compound with some similarity to tryptophan, in distilled water, it was indicated that the main mechanism of delineation of this acid was a complexation between the COOH groups and the soluble cationic forms of aluminum [28,33].

This is also consistent with the results of [34], where the removal efficiency of humic substances improves with increasing coagulant dose and with increasing initial humic substance content.

Lefebvre [35] indicates that aromatic compounds with at least two (identical or different) acid functions in the ortho position can be eliminated; it is the case of tryptophan acid.

The results obtained from our work confirm that the optimal dose of coagulant (aluminium sulfate) for the concentrations ($C_0 = 5, 10$ and 20 mg/L) and in the three types of water remained constant and equal to 80 mg/L .

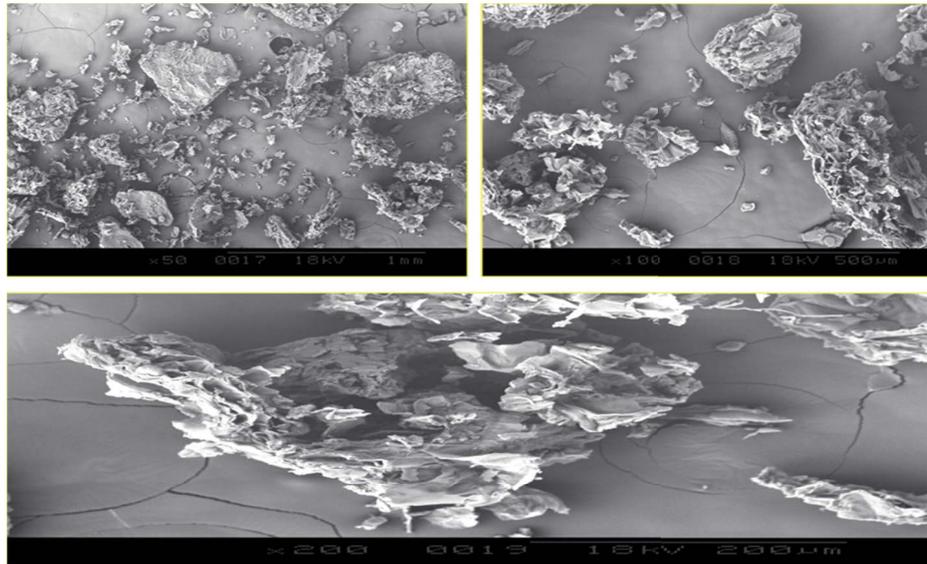


Fig. 7. SEM images of PB with 50–200 μm resolution.

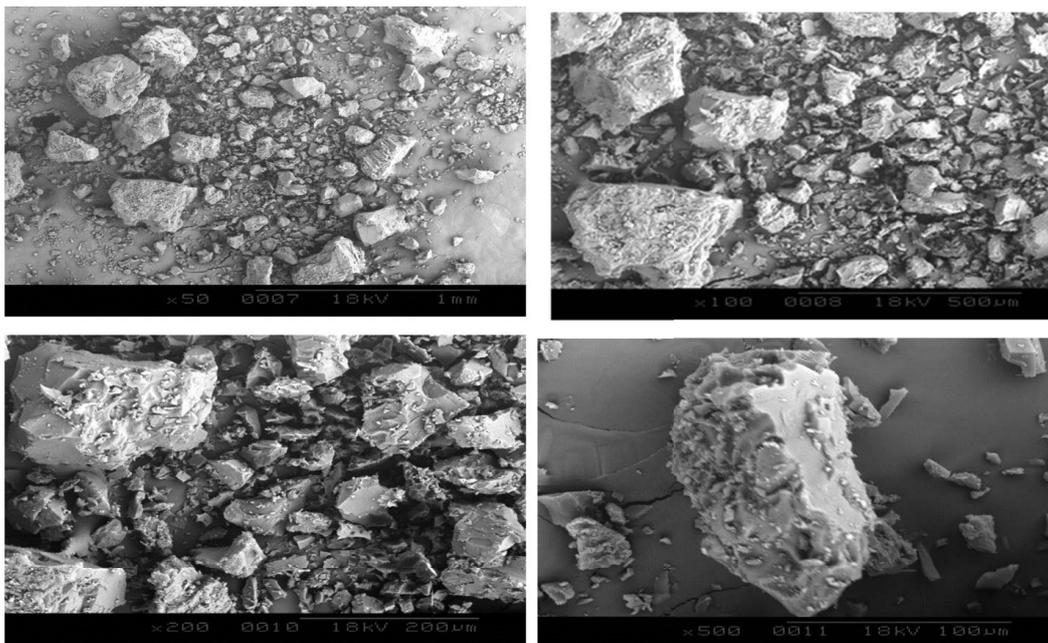


Fig. 8. SEM images of CAPB with 50–500 μm resolution.

3.4.2. Effect of the pH

The pH is an important parameter in the coagulation process, as it can change the surface charge of the coagulant and/or contaminant. Fig. 11 shows that the most suitable pH for these extracts to perform coagulation, was pH = 9 for tryptophan with removal yields (40.7%; 25.9%; 22.2%, $C_0 = 5\text{--}10\text{--}20\text{ mg/L}$).

Many works agree on the particularly determining role of pH in that it determines the electrical charge of organic and inorganic colloids in water, and is a factor determining the hydrolysis of aluminum salts. The organoaluminum

complexes formed during the reactions exhibit stability that is highly dependent on pH [36,37].

3.5. Study of adsorption coagulation-coupling

The second step was to study the behavior of tryptophan acid under the combined effect of aluminum sulfate with CAPB, with CAPP and finally with CAC.

As in the first experimental stage, the tests were carried out in distilled water, dam water and seawater, for different concentration values 5, 10 and 20 mg/L. Solutions

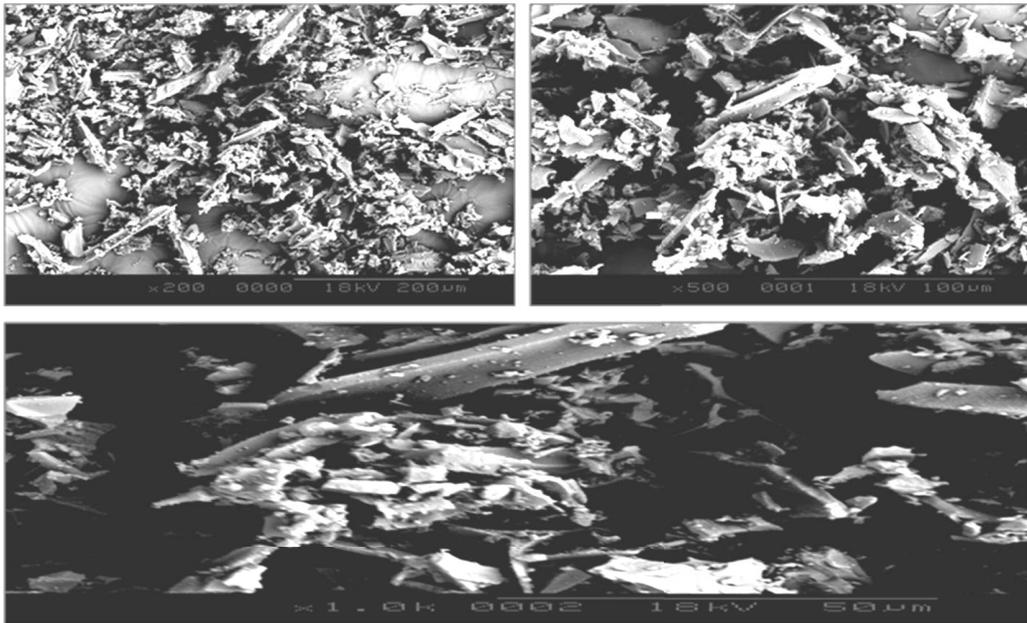


Fig. 9. SEM images of CAC with 200–1,000 μm resolution.

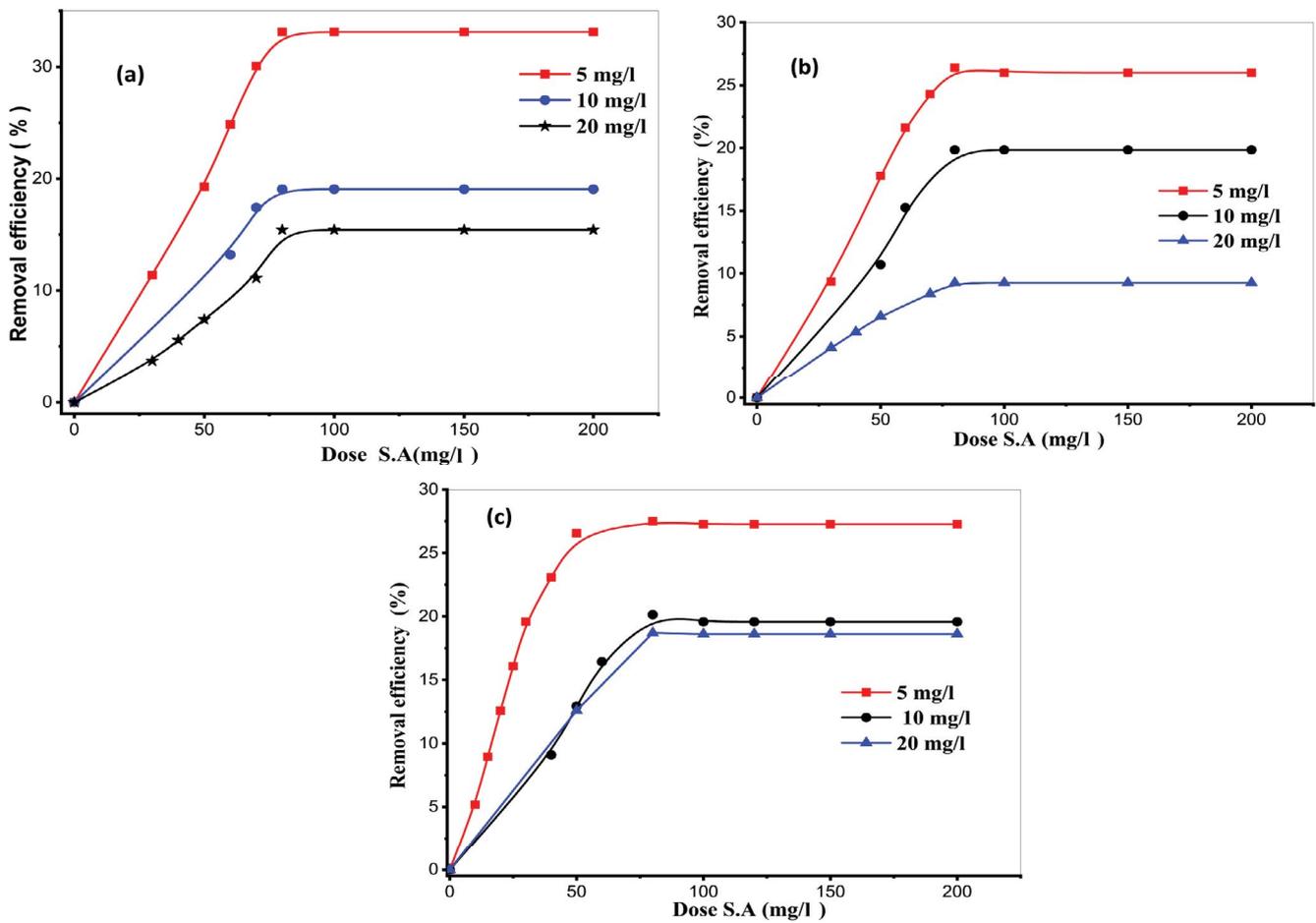


Fig. 10. Evolution of tryptophan removal efficiency $R\%$ as a function of the coagulant dose SA (mg/L), (a) in distilled water (pH = 7) for 1 h of settling, (b) in dam water for 1 h of settling, and (c) in seawater for 2 h of settling.

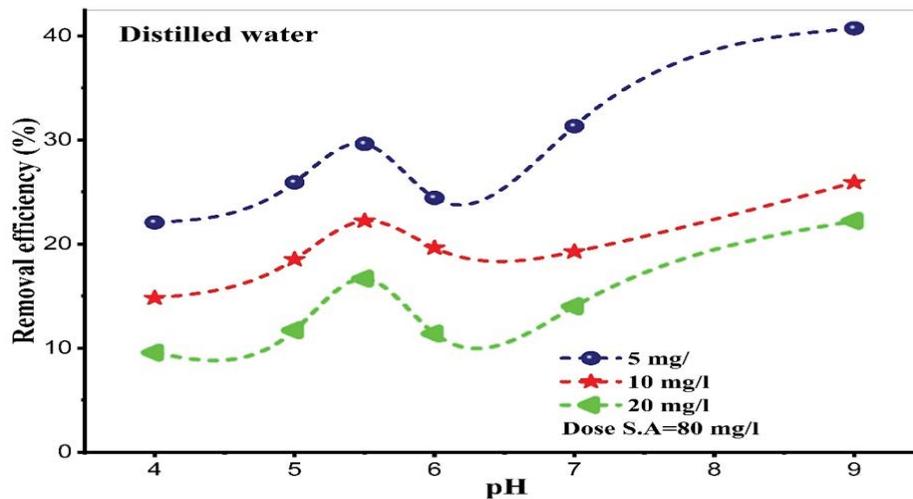


Fig. 11. Evolution of the removal efficiency as a function of the pH for the optimal dose of the coagulant ($T = 19^{\circ}\text{C} \pm 1^{\circ}\text{C}$; decantation 1 h).

of volume $V = 100$ mL at temperature $T = 19^{\circ}\text{C}$ were subjected to rapid stirring of 200 rpm for 3 min, then to 60 rpm for 0.5 h and finally to a settling of 1 h. Different reaction parameters were taken into account such as the dose of coagulant, of bean activated carbon (CAPB), of pea activated carbon (CAPP) and of CAC. In the three tests of aluminium sulfate combinations with each type of activated carbon CAC, CAPP and CAPB, the combination realized with a constant dose of aluminium sulfate equal to 80 mg/L corresponds to the optimal dose.

3.5.1. Effect of the CAC dose

The effect of the CAC dose on the removal efficiency of tryptophan is displayed in Fig. 12. For the three tested waters, in the presence of aluminium sulfate dose optimal equal to 80 mg/L, it is observed that the tryptophan removal efficiency increased with the mass of CAC, until reaching a plateau. This improvement in yields can be justified by the increase in the number of adsorption sites due to the increase in the mass of CAC with a specific surface area $S_{\text{BET}} = 721.3$ m²/g and pores of 71.96 Å in diameter. These results confirmed the efficiency of the CAC.

It is worth noting that the best yields were obtained when the CAC was combined to the aluminum sulfate, unlike the case of coagulation-flocculation using aluminum sulfate alone, where the maximum yields barely exceeded 30%.

In terms of interaction nature, the difference between the solute and the surface sites of the material concerns the total surface that is accessible to the solutes (porosity, specific area) accounting for the efficiency of the powdered activated carbon.

According to [38], the retention of organic matter on a porous solid depends on its own composition, the water chemistry and the characteristics of the activated carbon. The reaction mechanisms are essentially Van-Der-Waals forces, electrostatic forces and hydrogen bonds. In addition, the composition of organic matter is a complex set of molecules of varying sizes, with hydrophobic and hydrophilic groups.

It appears from Table 5 that the CAC combined to aluminium sulfate was effective in removing tryptophan from all waters considered, distilled water, dam water and seawater. The strong improvement in tryptophan elimination yield can be attributed to the retention of tryptophan molecules by the surface of the CAC.

Indeed, by studying the adsorption of tyrosine on different adsorbents, Bouchemal and Achour [39] found that the yield of tyrosine removal by powdered activated carbon is about 88% in an unbuffered medium.

From Fig. 13, an increase in the removal yield of tryptophan is observed as the pH of the solution increases. An optimal yield is obtained at pH = 9. The evolution of the elimination yield in the studied pH range is explained by the fact that when the pH is higher than pH_{pzc} the negatively charged CAC surface and the cationic tryptophan molecule in solution are positively charged. The adsorption can be considered by electrostatic interactions between the different charge of CAC and tryptophan. These interactions increase with pH increasing because the surface of the CAC becomes more and more negative when the solution becomes more and more basic.

3.5.2. Effect of the dose of CAPP

As observed in Fig. 14, for all tested waters, tryptophan removal efficiency increased with the mass of activated carbon of the pea peels, until reaching a constant value.

Before chemical activation, the specific surface area S_{BET} of the carbon prepared from the pea peels was around 1.17 m²/g. After activation, specific surface increased considerably to 735.27 m²/g, due to the number of adsorption sites increasing (pores).

It can be observed that the removal efficiency of tryptophan differed in the three waters. The difference most likely due to the saturation of the adsorption sites on the surface of the adsorbent, since an increase in concentration increases the number of molecules of the pollutant in the solution for the same mass of the adsorbent, which results

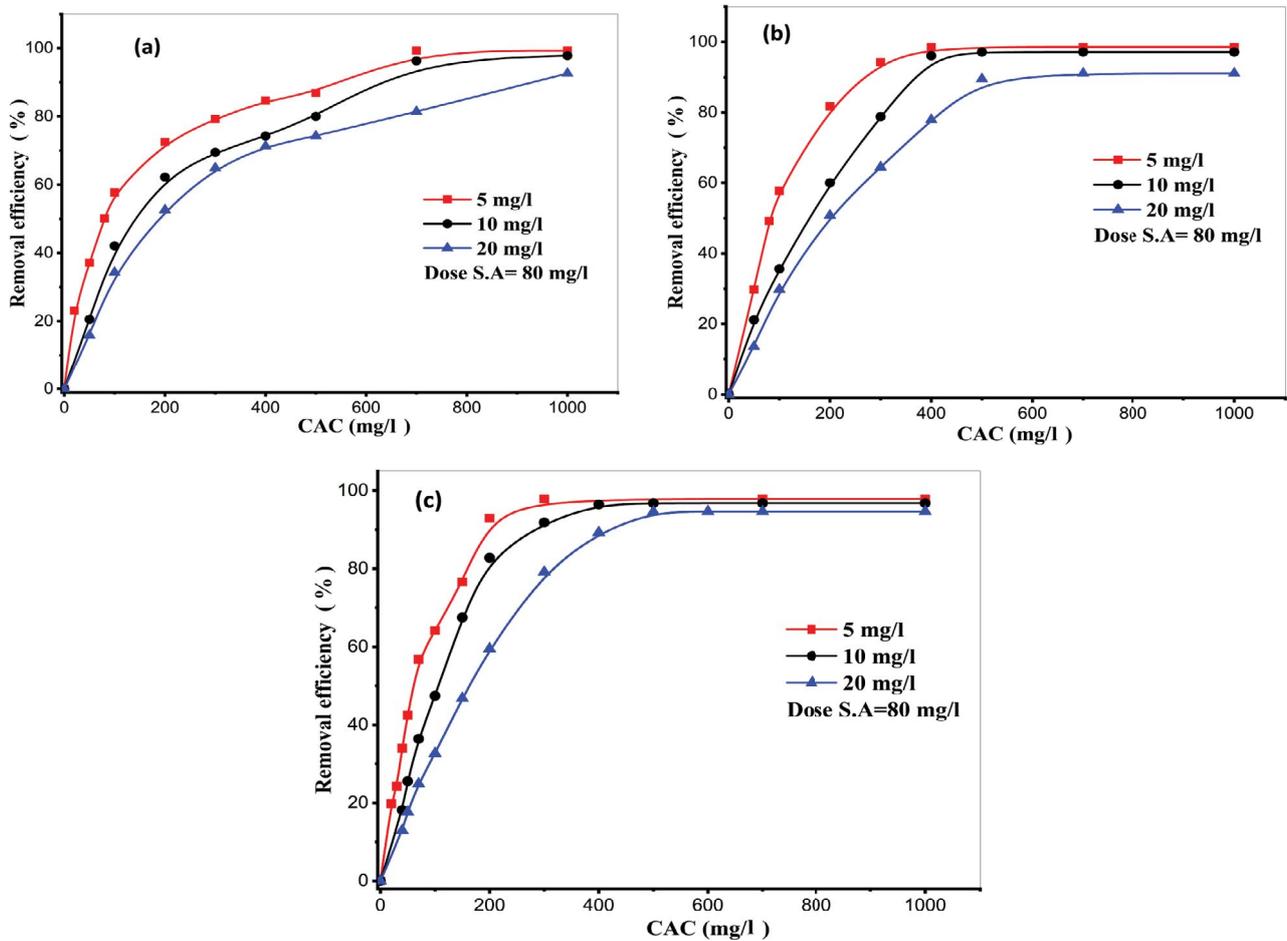


Fig. 12. Evolution of tryptophan removal efficiencies $R\%$ as a function of the CAC dose (mg/L), (a) in distilled water for 1 h of settling, (b) in dam water for 1 h of settling, and (c) in seawater for 2 h of settling.

Table 5
Maximum values of tryptophan removal efficiency as a function of the mass of commercial activated carbon

Concentration	Distilled water		Dam water		Seawater	
	m-CAC (mg/L)	$R\%$	m-CAC (mg/L)	$R\%$	m-CAC (mg/L)	$R\%$
$C_0 = 5$ mg/L	700	99.25	400	98.57	300	97.85
$C_0 = 10$ mg/L	1,000	97.77	500	97.14	500	96.78
$C_0 = 20$ mg/L	1,000	92.59	700	91.07	600	94.64

in a competition between the tryptophan molecules for the adsorption sites.

According to Gomri [40], the adsorption kinetics are rapid during the first few minutes, which may be explained by the availability of a large number of active sites on the surface of the material at the beginning of the adsorption process.

From Table 6 it can be said that CAPP improved the removal of tryptophan compared to coagulation alone.

The improvement of the coagulation-flocculation process was therefore ensured by the combination with adsorption.

It can also be noted that the yields of tryptophan removal in dam and seawaters were lower than in distilled

water. Since dam and seawaters contain compounds other than the target pollutant, the decrease in adsorption efficiency over time was due to the occupation of still vacant sites and to the appearance of repulsive forces between the molecules of the organic compound adsorbed by the materials and those in solution.

3.5.3. Effect of the dose of CAPB

As shown in Fig. 15, increasing the initial concentration led to a decrease in the removal efficiency by using the activated carbon from bean peels, for the three waters.

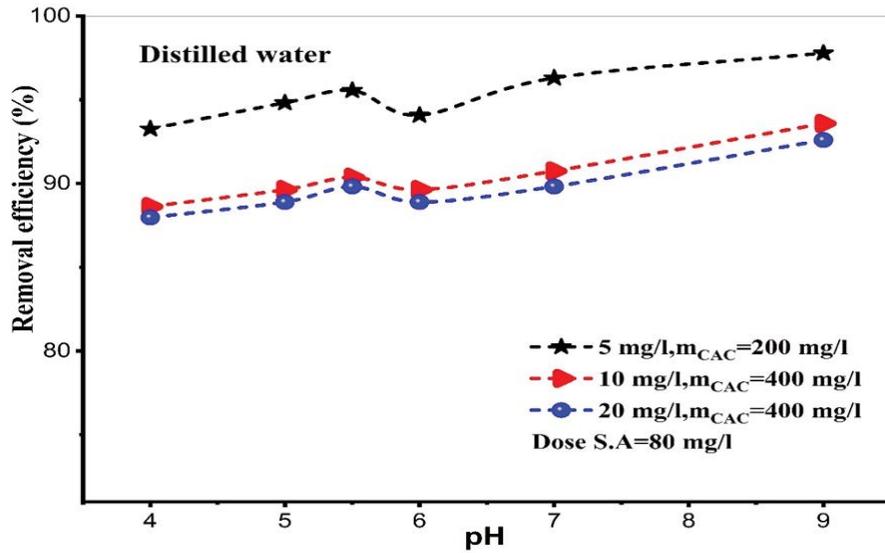


Fig. 13. Evolution of the elimination efficiency of tryptophan as a function of pH for the optimal dose of coagulant and the optimal mass of CAC ($T = 19^{\circ}\text{C} \pm 1^{\circ}\text{C}$; decantation 1 h).

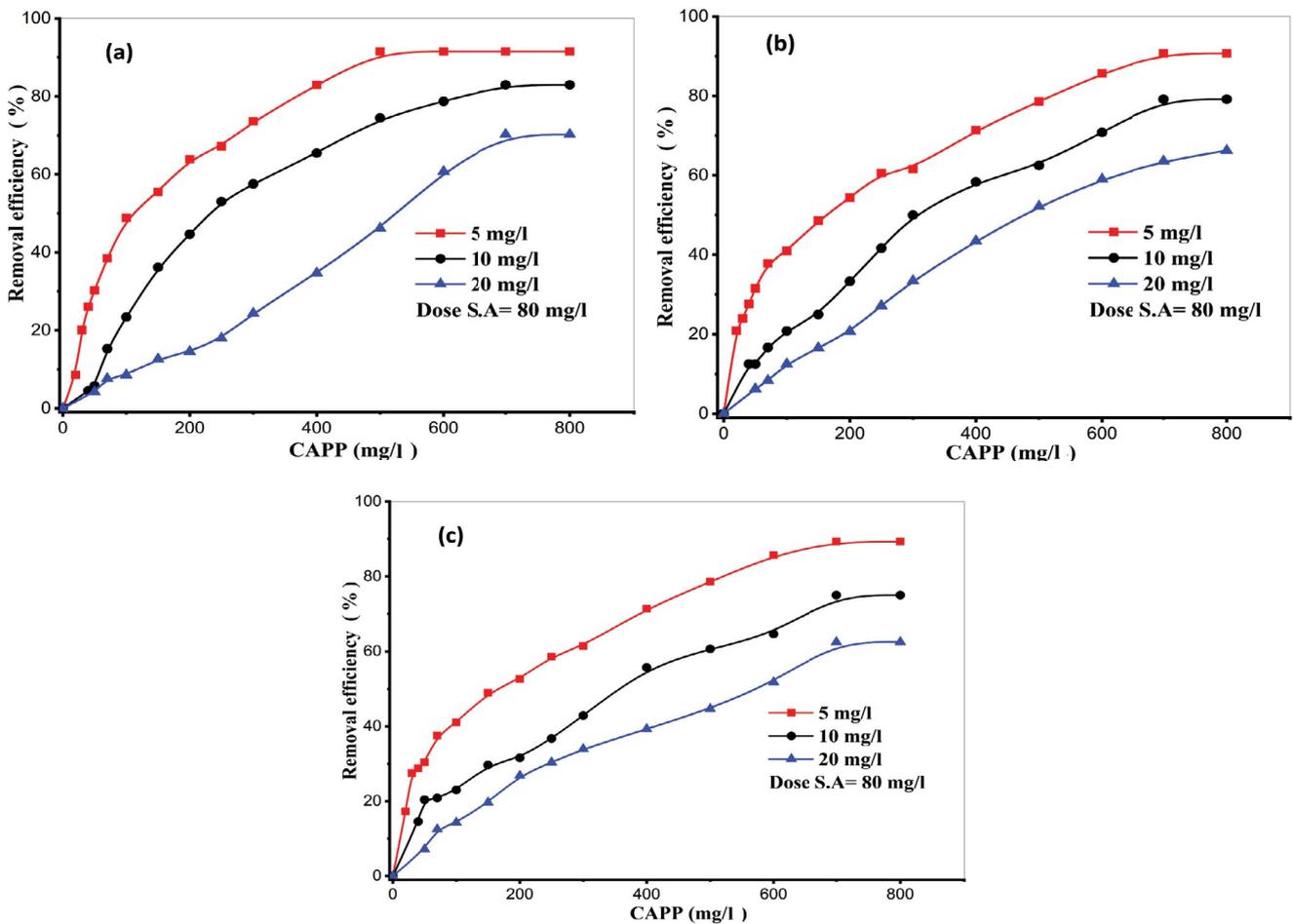


Fig. 14. Evolution of tryptophan removal efficiency $R\%$ as a function of the dose of pea peels activated carbon (mg/L), (a) in distilled water for 1 h of settling, (b) in dam water for 1 h of settling, and (c) in seawater for 2 h of settling.

Table 6
Maximum values of tryptophan removal efficiency as a function of the mass of pea peels activated carbon

Concentration	Distilled water		Dam water		Seawater	
	m-CAPP (mg/L)	R%	m-CAPP (mg/L)	R%	m-CAPP (mg/L)	R%
$C_0 = 5 \text{ mg/L}$	500	91.48	700	90.71	700	89.29
$C_0 = 10 \text{ mg/L}$	700	82.98	700	79.17	700	75.00
$C_0 = 20 \text{ mg/L}$	700	70.21	800	66.24	800	62.50

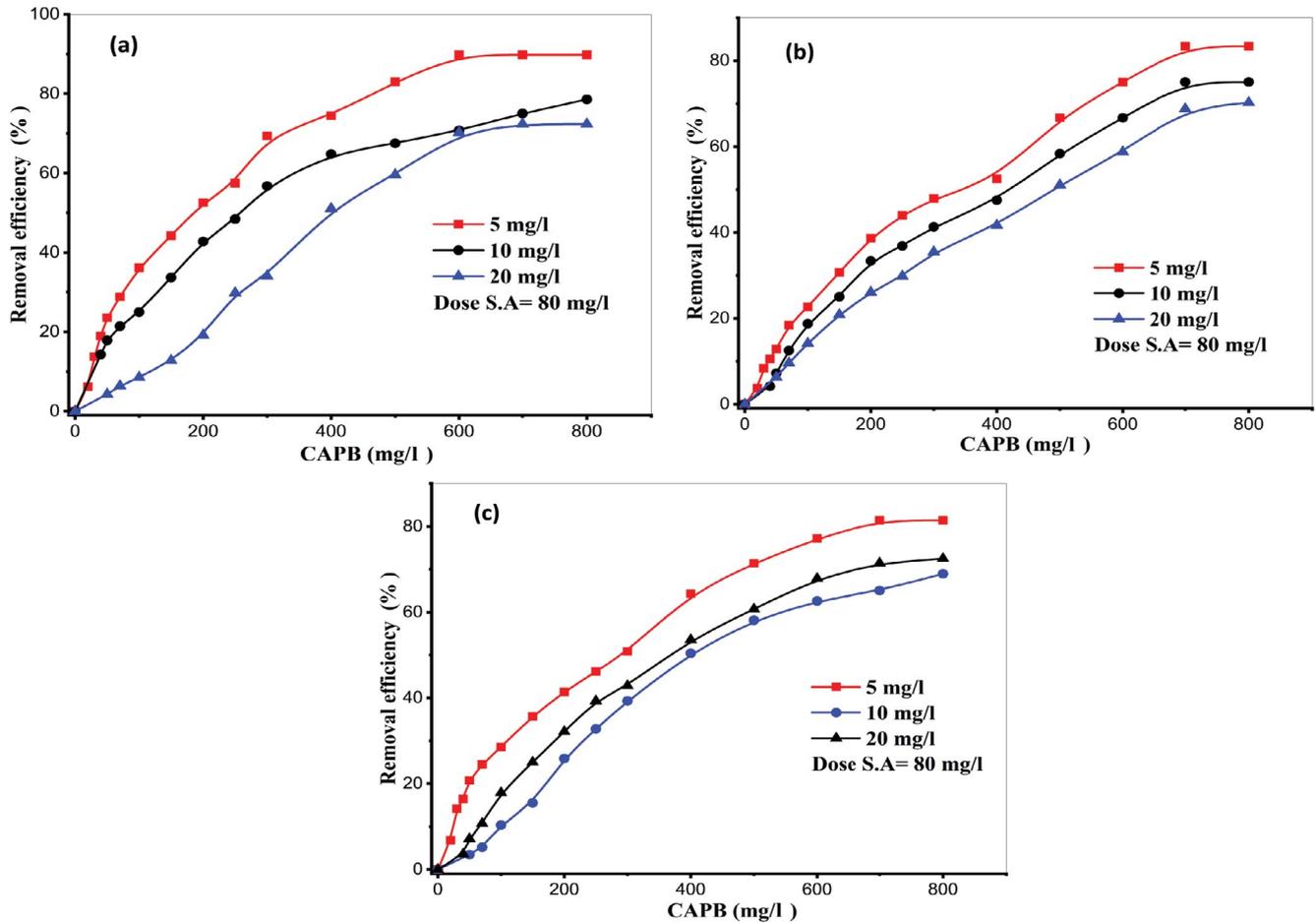


Fig. 15. Evolution of tryptophan removal efficiency $R\%$ as a function of the dose of bean peels activated carbon (CAPB) (mg/L); (a) in distilled water for 1 h of settling, (b) in dam water for 1 h of settling, and (c) in seawater for 2 h of settling.

The carbon that was prepared from bean peels has a specific surface area S_{BET} equal to $0.85 \text{ m}^2/\text{g}$, before the chemical activation. After activation, the specific surface area increases by up to $60 \text{ m}^2/\text{g}$, corresponding to an increase in the number of adsorption sites (pores), allowing an increase in the quantity of removed tryptophan.

The results of Table 7 show that the type of water significantly influences the elimination yields of tryptophan. Indeed, the maximum values of efficiency using CAPB differed from one water to another and are better for distilled water, because dam and seawaters contain molecules other than tryptophan. This process of increasing the surface area of the pores of the used materials makes it possible to achieve

good quality activated carbon with a very large porous structure and a large specific surface [29]. It is therefore very important to think about recovering agricultural waste to prepare activated carbons very useful in water treatment.

3.6. Comparison between the different results obtained for the three activated carbons (CAC, CAPP, CAPB)

The chemical activation by phosphoric acid H_3PO_4 leads to an increase in the specific surface ($760.56, 735.27, 721.3 \text{ m}^2/\text{g}$ for CAPB, CAPP, CAC) and the active sites on the prepared activated carbon. It is noted that the removal efficiency of tryptophan (either in distilled water, dam water

Table 7

Maximum values of tryptophan removal efficiency as a function of the mass of bean peels activated carbon (CAPB)

Concentration	Distilled water		Dam water		Seawater	
	m-CAPB (mg/L)	R%	m-CAPB (mg/L)	R%	m-CAPB (mg/L)	R%
$C_0 = 5$ mg/L	600	89.79	700	83.33	700	81.42
$C_0 = 10$ mg/L	800	78.57	700	75.00	800	72.50
$C_0 = 20$ mg/L	700	72.34	800	70.21	800	68.97

or seawater) by CAC is higher than the removal efficiency of tryptophan by activated carbon of pea peel (CAPP) and the removal efficiency by activated carbon of bean peel (CAPB), although the specific surface area of CAPB is higher than the specific surface area of CAPP and the specific surface area of CAC. These differences in the removal efficiencies of organic compound (tryptophan) can be justified by the pore size since the pore diameter of CAC is larger than the pore diameter of CAPP and CAPB (71.96, 58.42, 52.88 Å). From this we can conclude that pore size influences the adsorption capacity.

4. Conclusions

Different waters (distilled, dam and seawaters) loaded with tryptophan were tested in order to remove organic matter by coagulation-flocculation/adsorption.

The influence of some parameters such as the coagulant dose and the type of water on the tryptophan elimination was examined and analyzed. It appeared that the removal efficiency differed from one solution to another and the best yields were found in distilled water because dam and seawater contains molecules other than tryptophan. It was also observed that the removal efficiency of tryptophan increased with the dose of coagulant, and the optimal dose was 80 mg/L, from which yields remained constant.

The second stage of the experimental study focused on carrying out tests of coagulation-flocculation combined with adsorption, using CAC and activated carbon prepared from agricultural waste (bean peels, pea peels).

The study carried out between the various adsorbents tested showed that the activated carbon prepared from the plant base or the agricultural rejection leads to elimination efficiency ($R\%$) important for the tryptophan pollutant has a percentage of $R\%$ going to about an average between 70% to 90% for the carbon activated pea peels CAPP and a removal efficiency between 75% to 80% for carbon activated bean peels CAPB. By contrast, CAC has tryptophan removal efficiency up to an average of 98%. Then in short say that the CAPP and CAPB activated carbon having significant comparative and competitive elimination efficiency with CAC.

These results should be related to the fact that the size of the pore diameters of (CAC) was very large compared to the other adsorbents.

Activated carbon prepared from bean peels or pea peels is economical and effective material for removing organic matter because of its specific surface and its pore diameter. The results obtained showed that coagulation-flocculation, with aluminum sulfate alone, was not efficient, contrarily to

the combination between activated carbon and aluminum sulfate.

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