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Characterization of apricot stone shells as a rapid filter medium

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ABSTRACT

Two different size fractions of crushed apricot stone shells were prepared and characterized to investigate the use of this material in granular filters. Density, equivalent diameter, percent water absorption, sphericity, and bed porosity were determined to characterize the particles. Two different sets of leaching tests were performed to quantify the amount of organic matter released from apricot stone medium in water: (i) the amount of organic carbon that passes to water when the particles and water are contacted in a well-mixed batch container, and (ii) the organic carbon found in the filtrate of a fixed bed of apricot stone particles. The Ives' filterability test was employed to evaluate the effectiveness of removing particulates from a surface water as a function of apricot stone fraction size and coagulant dosage.

Keywords: Crushed shells of apricot stones; Filterability; Rapid filtration; Particle characterization

1. Introduction

Natural materials which are available in large quantities can be a good substitute for synthetic materials utilized for different purposes during water/wastewater processes. These processes include coagulation/flocculation, sorption processes (adsorption/absorption and ion exchange) and filtration. A number of researchers investigated the use of natural coagulants such as okra seed extracts [1], proteins extracted from mustard, red bean, sugar maize, and red maize [2,3] for coagulation-flocculation processes as an alternative to metal based coagulants. Adsorption of pollutants using natural materials is based on transformation of the material into a medium with a lot of exchange and/or adsorption sites through the use of an activation process. Some of the examples from recent studies include the use of oleaster and cherry to produce biochar for the removal of hexavalent chromium [4], plant biomasses to produce biosorbents for the removal of heavy metals [5], date palm wastes for the removal of synthetic dyes, phenolic compounds, pesticides and heavy metals [6], tamarind wood for the removal of lead [7], walnut shell for the removal of drugs [8].

Of particular interest in this work is the use of natural media in rapid filtration. While silica sand and anthracite coal have been used extensively as filter media in many industrialized countries, these materials may not always be readily available or they may not be the most economical choices in certain cases. As a result, many different media have been considered and used instead of sand and/or anthracite coal in countries such as Brazil, Chile, Colombia, India, the Philippines, and Korea [9]. These include materials such as crushed recycled glass, perlite, indigenous coals, crushed coconut shells, pea gravel, berry seeds, kernels of stone fruits, bituminous coal, and boiler clinker.

Crushed shells of apricot stones is considered in this work as Turkey is among the world's leading producers of apricots [10]. Total apricot production increased by 7.4% from 680,000 tons in 2015 to 730,000 tons for 2016 [11]. Apricot pit shell or apricot kernel shell accounts for approximately 10% of the fruit mass. The hard stone shell contains kernel, the seed. Considering these facts, Aksoğan et al. [12] investigated the use of crushed shells of apricot stones instead of anthracite coal in dual-media filters. Filtration experiments conducted on clay added tap water (a synthetic solution) without the use of a coagulant resulted in slightly better turbidity removal rates. It was also emphasized that there was no detectable deterioration in apricot

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stones during the course of the 4-months testing period. The main goal of this work is to further study the use of this material as a possible filter medium. Issues not addressed by these researchers are investigated.

2. Material and method

2.1. Characterization of materials

Apricot stone shells were obtained from a company in Malatya, Turkey. Bulk material was first subjected to a sieving process using a Ro-Tap sieve shaker (Retsch AS200 tap). Sieving process was carried out in accordance with ASTM standards [13]. The fractions tested in this study were 1.7–1.4 mm (representing a relatively coarse medium) and 1.18–1.00 mm sized particles (close to the size range widely used in rapid filters in Turkey). Each fraction was boiled and washed at least three times to remove the organic thin layer from their inner (concave side of) surfaces, oven dried (105°C) and stored (Fig. 1).

Particle size is one of the most important physical properties of a granular material since it has a direct influence on energy loss during filtration and the efficiency of processes such as turbidity and particle removal in the filters. Equivalent diameters of apricot stone shell fractions were calculated by i) counting and weighing 600 grains of each fraction, ii) calculating the volume of one grain using its particle density, iii) equating the volume of one grain to the volume of equivalent sphere.

The use of porous materials such as coal, activated carbon or other natural substances as adsorption or filter media has been the focus of numerous studies. However, the liquid (usually water) in contact with such materials penetrate the internal pores of the particles and the effective density of the particles is modified. A careful examination of past studies involving the contact of porous media with liquids shows that this fact has not been given careful consideration. Even when the presence of internal pores has been noted, it is usually not clear how properties such as particle density, particle size, shape, and bed porosity (excluding the internal pores of the particles) are measured in such cases. For example, fixed-bed head loss is very sensitive to porosity and yet internal pores of the media may be included in the calculated external bed porosity if particle density and the mass of the particle bed are not correctly determined.

Fig. 1. Apricot stone fractions used in the experiments.

This important point was addressed in a recent study [14] and it was demonstrated that the use of methods that ignore the penetration of water into the internal pores of the media will cause large errors in further calculations involving fixed and fluidized beds of such particles. Based on the findings of the aforementioned study, standard cone test [15] method was used for the determination of wet particle density of the apricot stone fractions used in this study.

Water permeability experiments were performed to determine sphericities of the two fractions. These experiments were conducted with an experimental set up that enables the measurement of head loss through a 20–25 cm depth of an apricot stone particle bed operating over a range of flow rates. Ergun [16] equation was then used for the determination of sphericities.

2.2. Organic matter release experiments

Fractions prepared as described above were tested to ascertain the extent of release of organic matter when they are in contact with water in two different arrangements (Fig. 2). To this end, two different sets of measurements were carried out to quantify the organic carbon release: (i) the organic carbon content in aqueous solutions where the particles and water were contacted in a continuously shaking constant volume container, and (ii) the organic carbon content of the filtrate passing through a fixed bed of apricot stone particles. Aqueous solution was replaced periodically with fresh, clean water during the shaker experiments whereas a continuous flow was passed through the bed of particles in the column experiments.

2.3. Filterability tests

Performance of a granular filter can be evaluated by inspection of the following: (i) filtrate quality, during both filter ripening and effective filtration stages, (ii) head loss generation, (iii) intervals between backwashes. In this study, the effectiveness of beds composed of apricot stone fractions was assessed by measuring Filterability Index (*FI*). Filterability test was proposed by Ives [17] and an apparatus (Armfield Co.) developed for this purpose was used in this study (Fig. 3). *FI* is expressed with the following formula:

$$FI = \frac{C}{C_0} H \frac{1}{V} \frac{1}{T} \tag{1}$$

where C is the filtrate quality, C_0 is the inlet water quality, H is the head loss (m), V is the filtration rate (m/h), T is the length of filter run (h).

FI is a dimension less number and low values of this number imply that a good filterability is achieved.

Raw water used in filterability tests was a surface water obtained from the inlet of a full scale drinking water treatment plant. Raw water with the turbidity (C_0) 12 ± 0.8 NTU was coagulated using ferric chloride ($FeCl_3{\cdot}6H_2O$) prior to filtration. Following vigorous and gentle mixing stages (15 s and 10 min, respectively), the sample was filtered through a bed of apricot stone particles (bed height = 4 cm and column diameter = 40 mm). According to the protocol proposed by Ives [17], the following data were recorded when the volume of filtered water was 1 L: total head loss,

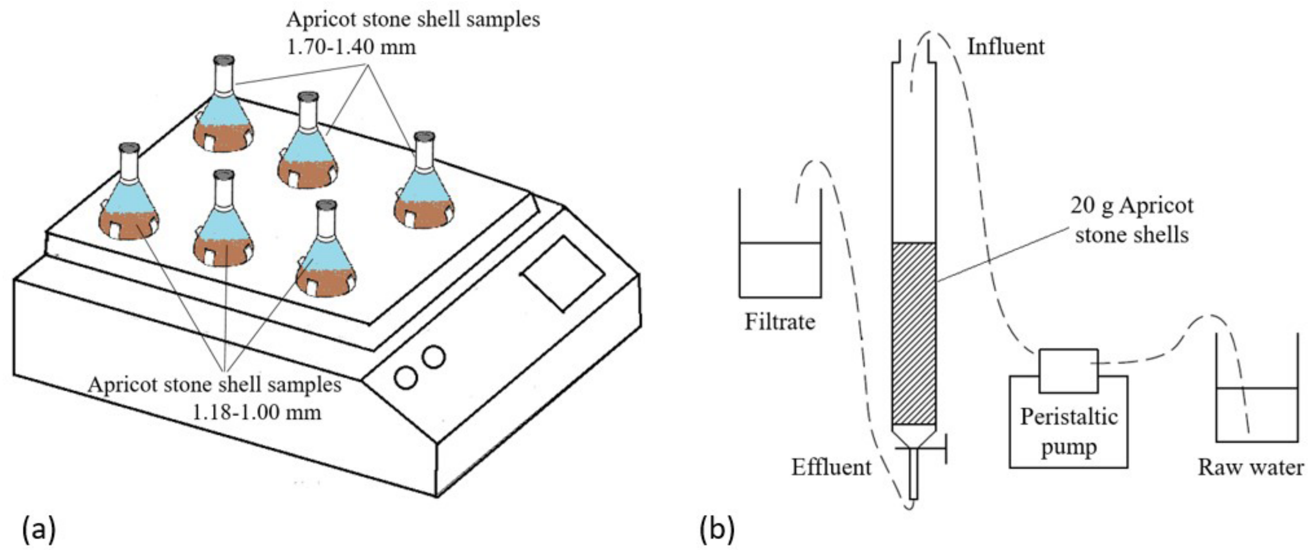

Fig. 2. The experimental setups for organic matter release tests (a) constant volume container experiments and (b) fixed bed filtration experiments.

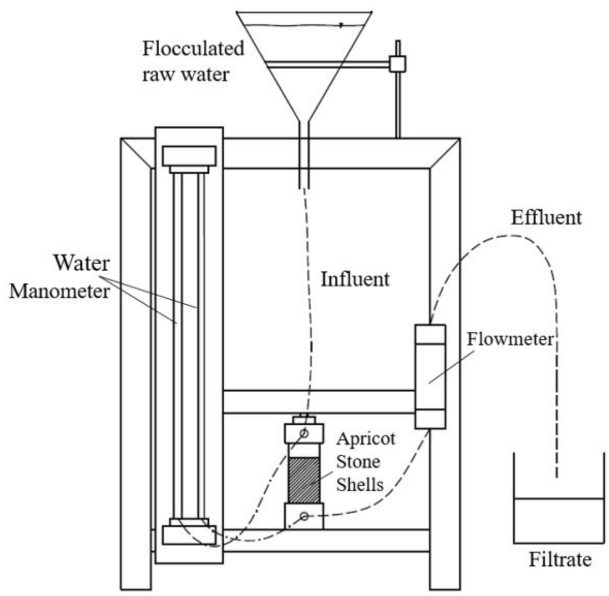

Fig. 3. The experimental setup used for filterability tests.

elapsed time to collect 1 L of filtrate and average turbidity of the filtered water. Filterability experiments were performed on five samples, four of which were pretreated with flocculation using ferric chloride, while the fifth one was filtered without the addition of any coagulant.

3. Results

3.1. Particle properties

Density, equivalent diameter and sphericity were determined according to the procedures described in an earlier publication [14]. A portion of each fraction was saturated with water and brought to a condition (referred to as the "saturated surface dry (SSD)" condition in the ASTM standard) so that the particle pores were filled with water but particle surfaces and the spaces between the particles were free of excess water [15]. Wet particle density was determined then by dividing this particle mass to volume of the SSD particles found by a water displacement method [14]. Wet densities and percent water absorption values are reported in Table 1. Wet particle densities are found to be approximately the same for the two fractions. Wet samples were then dried in an oven at 103–105°C and weighed to determine dry sample masses. Percent water absorption expressed as the percent increase in the mass of sample after soaking in water for 24 h (obtained as explained above) was calculated for each fraction. Water absorption values of apricot stone fractions were found to be around 30% (Table 1).

Table 1
Particle density and water absorption of apricot stone fractions

Sieve size	1.70–1.40	1.18–1.00
Density (kg/m^3)	1336.5	1340.3
Water absorption (%)	28.9	29.4
Bed porosity	0.521	0.524

It may be useful to note here that the skeletal densities (densities based on dry mass and skeletal volumes of the particles) were found to be 1482 and 1489 kg/m^3 for the 1.7–1.4 mm and 1.18–1.00 mm fractions, respectively. The density values reported in Table 1 may also be compared with the wet densities found by Yigit Hunce et al. [14]: They have reported the average wet particle densities of 1680, 1450 and 1965 kg/m^3 for anthracite, activated carbon, and zeolite, respectively. This shows that apricot stone is lighter than all of these materials (when all four are compared in the SSD condition which is the condition during water filtration and backwash operations). This information can be relevant when, for example, one has to consider any possible modification of backwash procedures if apricot stone medium is considered as a replacement for any of these materials.

Fig. 4 displays the volume equivalent diameters and sieve sizes used in preparation of these two fractions. The passing sieve size for a fraction is defined as the smallest sieve size through which that fraction passes, and the retaining sieve size is the largest sieve size that retains the fraction. A particle fraction can be prepared using standard sieves that differ by one size class. Particle size should be clearly defined in calculations for processes involving particles such as filtration, ion exchange and adsorption or absorption. In equivalent diameter computations, volume of one particle is found from dividing average mass of one particle to its density. For porous materials, wet (SSD) density determined experimentally as explained above and wet (SSD) mass calculated from dry mass and percent absorption values are used in this calculation. Equivalent diameters are found to be 1.77 mm for 1.7–1.4 mm fraction and 1.44 mm for 1.18–1.00 mm fraction (Fig. 4).

Sphericities were determined by measuring the fixed-bed head loss for each fraction and using the Ergun equation [16]. This calculation requires particle equivalent diameter and bed porosity values. Wet particle density is included in equivalent diameter calculations as explained above. Bed porosity is the ratio of volume of voids (or the difference between total bed volume and envelope volume of materials i.e. internal pores are not included in bed porosity) to the bed volume. Volume of materials was calculated using wet particle density and the mass of wet particles (pores filled with water) found by employing water absorption ratio of that fraction. Data obtained during permeability experiments are shown in Fig. 5. Sphericities of the 1.7–1.4 mm and 1.18–1.00 mm fractions of apricot stones were found to be 0.70 and 0.69, respectively. These values are the mean values of several measurements (Fig. 5).

3.2. Organic carbon release

In a solid-liquid system operated either in a batch or a continuous-flow mode, a solid surface will always be in contact with the liquid. In this study, the only pretreatment method applied was boiling and washing for the removal of the organic thin layer attached to apricot stone shells. Therefore, leaching tests were performed to quantify the amount of organic matter released from apricot stone shells in water. This is needed to determine if a significant amount of organic matter will be released to the water during filtration. This will be an important consideration especially in a drinking water treatment application. These experiments were conducted in two different arrangements: constant volume (batch) and continuous flow experiments.

Fig. 6 shows the results of batch experiments. The data represent averages of the results of three replicates for each fraction. "Organics release" was computed as follows: (i) Approximately 20 g of grains were contacted with 100 mL of deionized water for a definite period of time such as 1 d. (ii) A representative sample was taken from the solution and its total organic carbon (TOC) concentration was determined with a TOC analyzer (GE Sievers M5310C). (iii) Rate of organic matter release was found by dividing the amount of organic carbon (concentration times volume of the solution) to the mass of grains in that container and duration of contact.

As seen from Fig. 6, the organic carbon release decreases with time rapidly during the first 10 d (most of the release occurring within the first 2–3 d) and then continues to decrease at a slower rate. This indicates that such filters may have to be operated with an extended initial washing and/or a filter-to-waste period after the initial loading of the filter media. The length of this period, however, may

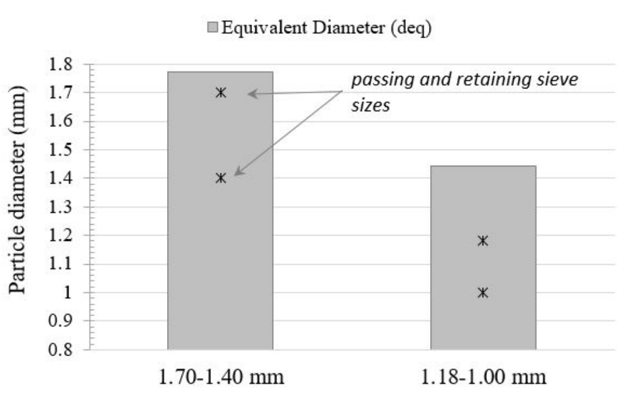

Fig. 4. Particle equivalent diameter based on wet particle density.

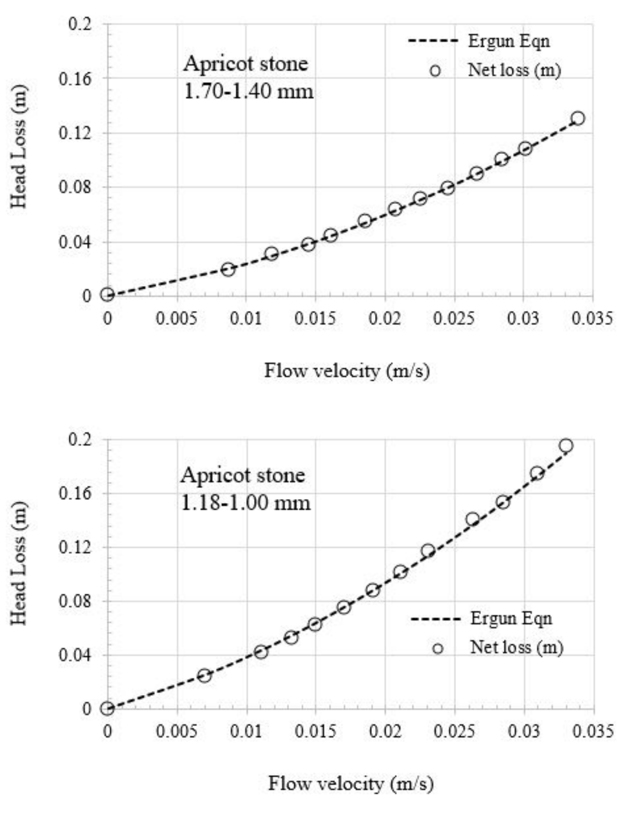

Fig. 5. Fixed-bed head loss data for apricot stone fractions.

be much shorter than would be discerned from this figure which was obtained with batch tests.

Results of continuous flow experiments are given in Fig. 7. Deionized water was passed through a column (2.2 cm in diameter) containing 20 g of apricot stones. Total organic carbon concentration was measured in samples collected from the effluent of the column operated at a filtration rate of 5 m/h. Samples were collected at various times (ranging between 5–30 min) during the experiment. Fig. 7 displays the average effluent TOC concentration for the time period ending at the time displayed on the horizontal axis. For example, the average effluent TOC concentration between 29.3 and 43.9 bed volumes was 59.4 mg/L in the experiment with 1.7–1.4 mm fraction. Put in other words, this is not an instantaneous value but an average over the (43.9 – 29.3 = 14.6) bed volumes that passed through the column since the last measurement. Fig. 7 shows that a filter containing crushed shells of apricot stones would not significantly increase the organic content of the treated water after an initial period (in this case, about 200 bed volumes) during which most of the organic carbon release takes place.

3.3. Results of filterability experiments

Data collected during the filterability tests are shown in Figs. 8–10. Fig. 8 shows that turbidity removal efficiency increases as coagulant dosage is increased. Here a 20 µM corresponds to 5.4 mg $FeCl_3 \cdot 6H_2O$ per liter of solution. Fig. 9 shows the corresponding total head loss values. It is seen that, as expected, head loss increases as coagulant dosage is increased. It may be difficult to determine the best coagulant-medium combination looking at these two figures only. FI values shown in Fig. 10, however, may be helpful in such a decision. It should be remembered that lower FI values are in general more desirable. It is seen that the decrease in FI as dosage is increased from 60 µM to 80 µM is marginal for both of the fractions and the use of 60 µM coagulant could

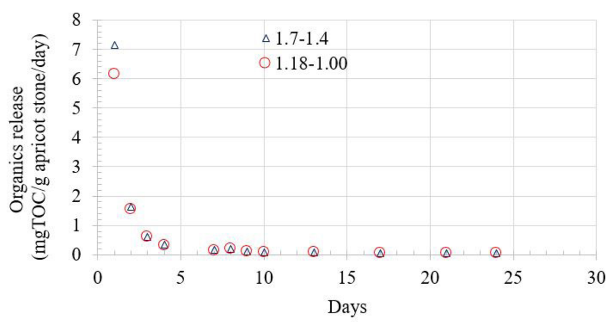

Fig. 6. Total organic carbon content in samples contacting with apricot stone particles at constant temperature and constant volume.

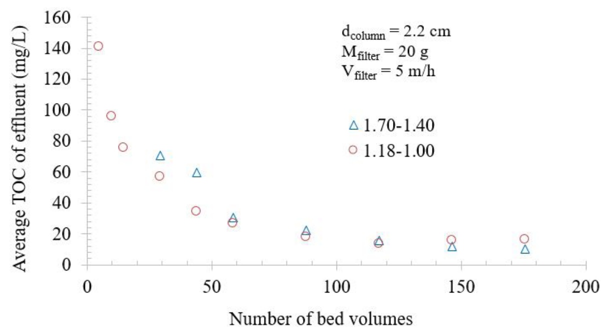

Fig. 7. Total organic carbon content in samples taken from the effluent of filter bed containing apricot stone shells.

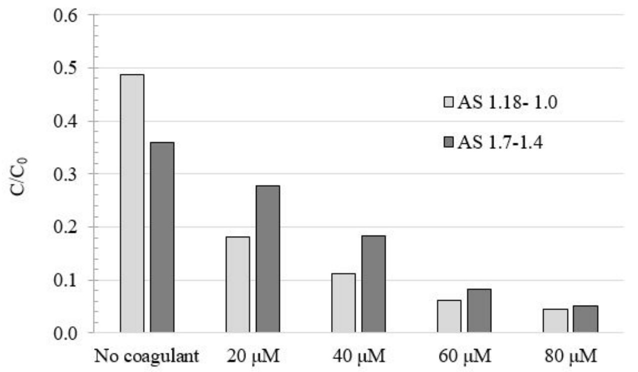

Fig. 8. Relative effluent concentration.

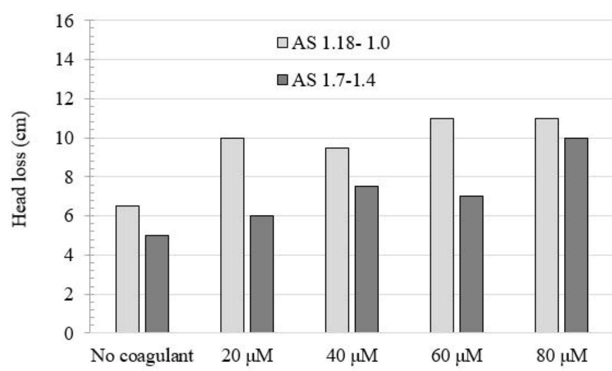

Fig. 9. Total head loss across the bed.

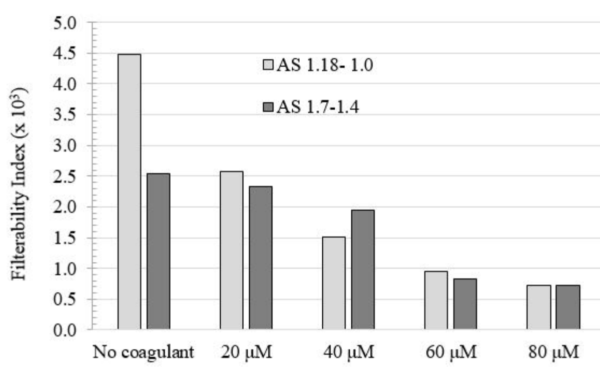

Fig. 10. Filterability Index (FI).

be recommended in this case as a preliminary decision. It is also seen that although the finer fraction produces slightly better effluent quality (as would be expected from filter theory) in all the tests with a coagulant, the two fractions yield similar FI values at this coagulant dosage. This is because the coarser fraction produces lower head losses (see Fig. 9). It is also seen that the difference between the FI values for the two fractions decrease as coagulant dosage is increased.

4. Conclusions

The conclusions and contributions of this study can be summarized as follows:

- Crushed shells of apricot stones are considered as a rapid filter medium.
- Two fractions of apricot stones are prepared and their physical properties are determined. It is explained that, for a porous material like apricot stones, all properties (diameter, density, particle shape, bed porosity) should be based on the SSD (saturated surface dry) condition.
- An important consideration in the application of this material to filtration is the possibility of organic matter release to the filtrate. Two different (one batch, one column) tests were carried out for each of the fractions to determine organic matter release as a function of time.
- It is found that significant amounts of TOC are released during the initial periods of contact between apricot stones and water. Although this issue should not cause a concern in applications involving wastewater filtration, it should be considered carefully in drinking water filtration. Extended initial washing and possibly an initial period of filter-to-waste operation may be necessary when this material is employed.
- Ives' Filterability Index test was applied to two fractions of apricot stones. This test may be a useful tool for a preliminary and quick evaluation of variables such as coagulant type, dosage, filter medium size, and filtration rate, although it cannot be expected to replace pilot-scale testing.

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