Coconut endocarp and mesocarp as both biosorbents of dissolved hydrocarbons in fuel spills and as a power source when exhausted

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ABSTRACT

Health and environmental problems associated with the presence of toxic aromatic compounds in water from oil spills have motivated research to develop effective and economically viable strategies to remove these pollutants. In this work, coconut shell (endocarp), coconut fiber (mesocarp) and coconut shell with fiber (endocarp and mesocarp) obtained from coconut (*Cocos nucifera*) waste were evaluated as biosorbents of benzene, toluene and naphthalene from water, considering the effect of the solution pH (6 – 9) and the presence of dissolved organic matter (DOM) in natural water (14 mg/L). In addition, the heat capacity of saturated biosorbents was determined to evaluate their potential as an alternative power source to conventional fossil fuels. Tests of N_2 physisorption, SEM, elemental and fiber analysis, ATR-FTIR and acid-based titrations were performed in order to understand the materials' characteristics, and to elucidate the biosorbents' hydrocarbon adsorption mechanism. Coconut fiber showed the highest adsorption capacities (222, 96 and 5.85 mg/g for benzene, toluene and naphthalene, respectively), which was attributed to its morphologic characteristics and to its high concentration of phenolic groups, associated with the lignin structure. The pH of the solution did not have a significant influence on the removal of the contaminants, and the presence of DOM improved the adsorption capacities of aromatic hydrocarbons. The adsorption studies showed biphasic isotherms, which highlighted the strong affinity between the molecules adsorbed on the biosorbents and the aromatic compounds remaining in the solution. Finally, combustion heat analysis of coconut waste saturated with soluble hydrocarbons showed that the heat capacity increased from 4407.79 cal/g to 5064.43 ± 11.6 cal/g, which is comparable with that of woody biomass (3400-4000 cal/g); this waste biomass with added value could be a promising biofuel.

Keywords

Biosorption; Coconut waste; Aromatic interactions; Aromatic hydrocarbons; Two-steps isotherms; Energy production

1. Introduction

Aromatic hydrocarbons enter the environment through anthropogenic activities such as crude oil spills, burning fossil fuels and fuel leakages (Foght, 2008). These hydrocarbons are comprised of simple aromatic compounds (monocyclic) such as benzene and toluene, polycyclic aromatic hydrocarbons (PAHs) such as naphthalene and pyrene, and isomers with countless alkyl substituents (Flores-chaparro et al., 2016; Foght, 2008). Annually, aromatic compounds impact environments such as groundwater, surface freshwater bodies, soils and terrestrial and marine sediments (Ali and Abdoul-Enein, 2004; Foght, 2008), causing damage to flora, fauna and humans. For example, the consumption of water containing aromatic compounds may cause in the human population: anemia, problems in the nervous system, kidney or liver, as well as increased risk of cancer (WHO, 2011). Therefore, it is important to contribute to the development and understanding of the techniques that are the most appropriate to remove aromatic compounds from water. The adsorption process is a feasible technique for the removal of several pollutants (Ali and Gupta, 2006). A wide variety of adsorbent materials have been used to remove organic pollutants from water, including activated carbon, zeolites, activated alumina and polymeric resins (Ali et al., 2012; Flores-chaparro et al., 2016). In recent years, the use of low-cost materials, among them biomass, is considered a promising alternative for replacing conventional adsorbents to remove organic compounds from water (Abdolali et al., 2014; Fomina and Gadd, 2014; Michalak et al., 2013; Tran et al., 2015). Biosorption is the property of certain types of biomass to concentrate on its surface certain molecules or ions from aqueous solutions (Volesky, 2007); basically, a low-cost biosorbent requires little processing, is abundant in nature or is a byproduct or waste from any industry or process (Fomina and Gadd, 2014). Additionally, the disposal of exhausted biomass is usually a problem; hence, its reuse is crucial for a cost-effective process. Its combustion could be a viable alternative to conventional fossil fuels (Almendros et al., 2015; Ronda et al., 2016), moreover, it is

known that biomass can become one of the most valuable sources to reduce pollution emissions from energy production processes (Ronda et al., 2016).

The use of agricultural waste from the coconut *(Cocos nucifera)* has received attention as an effective adsorbent due to its low cost, high potential to remove several water contaminants and as an energy resource due to its high carbon content and fuel value (Yerizam et al., 2013). Moreover, the physical characteristics of the pristine material allow it to be used directly in adsorption processes in packed-bed columns on an industrial scale, or in reactive permeable barrier (PRBs) technologies for sustainable in situ remediation of contaminated groundwater. Coconut-based adsorbents have been applied mainly in the removal of metals (Conrad and Bruun, 2007; de Sousa et al., 2010; Mohan et al., 2006; Parab et al., 2008; Selvi, 2001), dyes (Gupta et al., 2010; Hameed et al., 2008a; Kavitha and Namasivayam, 2008; Sureshkumar and Namasivayam, 2008; Vieira et al., 2009), phenol compounds (Hameed et al., 2008b; Sathishkumar et al., 2007; Tan et al., 2008), inorganic anions (Namasivayam and Sangeetha, 2008, 2006; Namasivayam and Sureshkumar, 2007) and radionuclides (Anirudhan et al., 2009; Bhatnagar et al., 2010; Parab and Sudersanan, 2010). In addition, since the coconut waste is produced in large quantities in several countries, e.g., Indonesia, the Philippines, India, Brazil, Mexico, among others (CONACOCO, 2012), these are widely available and therefore it is important to analyze strategies to valorize them as biosorbents and also the exhausted biosorbents, as a power source such as an alternative to fossil fuels.

Reports regarding the removal of aromatic hydrocarbons from aqueous solutions using biosorbents are scarce (Agarry et al., 2013; El-gendy and Nassar, 2016; Nduka et al., 2008; Sanchez-Galvan et al., 2013; Wahi et al., 2013; Younis et al., 2015; Zhang et al., 2014). Owabor and Agarry, (2014) investigated the use of coconut shell for the removal of naphthalene and pyrene from synthetic wastewater considering the variation of adsorbates, dose of adsorbent, the particle size and the stirring time. The maximum adsorption capacity for naphthalene obtained by the Langmuir model was 24.3 mg/g. The authors did not show data on the characterization of the material, neither was an

adsorption mechanism proposed. To the best of our knowledge, there are no studies reporting either the removal of benzene and toluene from aqueous solutions by coconut waste, or the assessment of the exhausted biosorbents to be used as a power source.

According to the above, the main objective of this study was to assess, in batch studies, the removal efficiency of benzene, toluene and naphthalene from water, by using the mesocarp and endocarp of coconut waste as biosorbents, and to determine the suitability of hydrocarbon-loaded coconut biosorbents for energy production by combustion. For this purpose, the biosorbents were physically and chemically characterized, the enthalpy of adsorption was experimentally determined and the heat of combustion of exhausted materials was acquired. Since the pH of natural waters should be between 6.5 and 8.5, and the fate of organic contaminants in aquatic environments can be altered by their interactions with complex mixtures such as dissolved organic matter (Xiao et al., 2014), the effect of pH and dissolved organic matter on the removal of aromatic compounds was also evaluated.

2. Materials and methods

2.1. Materials

Coconut residues were obtained from a local seller in San Luis Potosi, Mexico, and their fractions were divided into: the hard part (endocarp-coconut shell), the fibrous part (mesocarp-coconut fiber) and a combination of both (coconut shell with fiber), which were designed as CsF, F and CcF, respectively. The coconut shell was ground and sieved to get a particle size between 0.5 and 1.7 mm and the fibers were standardized to a size of approximately 1 cm. These materials were washed with deionized water until colorless water was obtained. Finally, the biosorbents were dried in an oven at 50 °C for 48 hours, and were stored in polyethylene bags until the experiments were carried out.

2.2. Biosorbent Characterization

The surface area and pore size distribution of the biosorbents were obtained by N_2 physisorption employing a surface analyzer (Micromeritics ASAP 2020). The samples were outgassed at 40 °C for 12 hours. The morphology of the endocarp and mesocarp was observed by a field emission scanning electron microscope (FEI Quanta 200 Environmental SEM) equipped with a BSD detector, operated at 20-25 kV and a working distance of 10 mm; the samples were coated with a layer of gold before the microscopic examination. The elemental analysis was done in an Elemental Combustion System (COSTECH Model 4010), using 0.5 mg of each biosorbent. The main lignocellulosic fractions in the coconut waste were quantified by using a fiber analyzer (ANKOM 200). The procedure was based on the sequential extractions method proposed by (Van Soest, 1963). The point of zero charge (pH_{PZC}) and the quantification of functional groups were obtained through potentiometric titrations (Velazquez-Jimenez et al., 2013) by using NaCl 0.01 M as a supporting electrolyte; the data were analyzed by using SAIEUS program. Finally, ATR-FTIR spectroscopy (Thermo Nicolet Nexus 470 FT-IR) was performed to identify the functional groups present in the biosorbents, the spectra were obtained in the range between 500 and 4000 cm^{-1} with 4 cm^{-1} of resolution and 64 scans averaged.

2.3. Aromatic Hydrocarbons Adsorption: Equilibrium and Kinetics Experiments

The hydrocarbon solutions used for equilibrium and kinetic experiments were prepared, based on the solubility reported (Flores-chaparro et al., 2016), within the range of 3.6-30 mg/L, 60-500 mg/L and 213-1780 mg/L for naphthalene, toluene and benzene (Sigma Aldrich, 99% purity), respectively. 0.05 g of CsF, CcF (10% fiber weight), or 0.015 g of F were contacted with 0.025 L of solution in amber glass containers and then closed with Teflon caps, with no free headspace to avoid volatilization. The bottles were kept at 25 °C and 110-120 rev/min for two days. The influence of initial pH in the adsorption process was investigated within the pH range of 6-9 for

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each chemical compound. All tests were done in duplicate. Moreover, adsorption kinetics were performed using a total of 15 bottles for every solution, and at given time intervals a bottle was sampled. The equimolar kinetics were performed using a stock solution with a concentration of 195 µM of each studied compound. The effect of dissolved organic matter in the adsorption process was performed by using natural water from a reservoir located in San Luis Potosi, Mexico. The adsorption capacity of the biosorbents (q_e, mg/g) was calculated as follows:

$$q_e = \frac{V(C_o - C_e)}{W} \qquad (1)$$

where V is the total solution volume (L), W is the mass of adsorbent (g), and C_o and C_e are the initial and final (at equilibrium) hydrocarbon concentrations (mg/L), respectively.

2.4. Enthalpy of Adsorption

The heat of reaction during the hydrocarbon adsorption process by CcF was determined. For this, 0.5 g of the dry biosorbent was contacted with 100 mL of benzene, toluene or naphthalene with concentrations of 1780, 500 and 30 mg/L, respectively. From the registered temperature increase, according to the analytical method described in Section 2.6, the enthalpy change was calculated using the following formula:

$$\Delta H_T = \frac{-(\Delta Tc)(e)}{m} \qquad (2)$$

Where ΔH_T is the enthalpy change; **e** is the standardized equivalent energy of the calorimeter; ΔTc is the temperature increase during the reaction and **m** is the mass of the biosorbent.

2.5. Determination of combustion heat

The biosorbent CcF impregnated with hydrocarbons, i.e., resulting from the adsorption equilibrium experiments at the highest concentrations (1780, 500 and 30 mg/L of benzene, toluene and naphthalene, respectively) were dried for 24 h at room temperature, and then for 1 extra hour in a

stove at 40 ºC. At the same time, controls were run consisting in the biosorbent CcF contacted to deionized water under the same conditions as the adsorption experiments. Then, approximately 45 mg of the dry biosorbent (control or hydrocarbon treated biomass) were combusted in a 1109A Semi-Micro Oxygen Combustion Vessel (Parr Instrument Company), as described in Section 2.6.

2.6. Analytical Procedures

The concentrations of benzene, toluene and naphthalene were determined by an UV-Vis (Thermo Aquamate) spectrophotometer at wavelengths of 254, 261 and 284 nm, respectively. The concentration of the same compounds in the equimolar experiments was determined by a high-performance liquid chromatograph (HPLC Agilent 1260), equipped with a photodiode array detector and reversed phase column C-18 (Phenomenex Gemini), at a wavelength of 200 nm. The injection volume was 15 µL and a mixture of acetonitrile-water (80: 20/V:V) was used as the mobile phase at a flow rate of 0.5 mL/min. The experimental enthalpy change was analyzed by using a 6755 Solution Calorimeter (Parr Instrument Company). The natural water was analyzed by ICP-OES (Varian 730-ES) to determine metals concentration, by capillary electrophoresis (Agilent 1600) for anions concentration, and by a Total Organic Carbon Analyzer (TOC-VCSN SHIMADZU) to obtain the total organic carbon concentration. The heat of combustion of the biosorbents was determined by using a 6725 Semi-micro Calorimeter (Parr Instrument Company) under an O_2 atmosphere at 3 Mpa (99.5 % purity).

3. Results and discussion

3.1. Surface Area and Pore Size Distribution

The pore volume of all biosorbents was less than 1.2×10^{-3} cm^3/g, which is formed mainly for mesopores and macropores, and was much lower with respect to a porous material such as activated carbon (Nieto-Delgado et al., 2011). It is known that the development of a porous structure and surface area is carried out -during the activation process of a material (Cooney, 1999). In this case,

the low pore volume that was observed in the samples (Table 1) is common for biosorbents since they are materials without pretreatment to increase their porosity (Nieto-Delgado et al., 2011). The values of BET surface area for CsF (0.4 m^2/g) and CcF (0.41 m^2/g) are very similar to those reported for coconut shell by Acheampong et al., (2011), 0.4 m^2/g, and Singha and Das, (2012), 0.52 m^2/g. The value for F (0.751 m^2/g) was almost double that of CsF and CcF; Acheampong et al., (2011) who also reported a similar value (0.9 m^2/g) for coconut fiber.

Materials with a high surface area and pore volumes do not necessarily have the best adsorption capacities (Garcia-Reyes and Rangel-Mendez, 2010), and it is important to consider others factors that can influence the adsorption process such as surface charge distribution, functional groups and the morphology of the material (Cooney, 1999). In this regard, the morphology of coconut shell and fiber was explored by microscopy. The micrograph of the coconut shell (Fig. S1-A) shows a smooth surface with few pores and the micrograph of coconut fiber (Fig. S1-B) presents an internal tubular hollow structure, which is why this has the greatest surface area.

3.2. Fiber and Elemental Analysis

The main components of coconut-based biosorbents are cellulose, hemicellulose and lignin, which are the primary cell wall components (Ochoa-Villarreal et al., 2012). Also, lignocellulosic materials can have small amounts of pectin, protein, vitamins, carbohydrates, enzymes, water, lipids and ash (Tran et al., 2015; Velazquez-Jimenez et al., 2013). In this study, no significant differences in lignocellulosic components were found between each coconut fraction (Fig. S2). Moreover, it is known that soluble compounds (10-11%) are mainly composed of proteins and sugars, and cellulose is the major constituent of plant cell walls (Ochoa-Villarreal et al., 2012) as found in the three coconut fractions (40-42%), and finally the hemicellulose content (23-25%) was quite similar to lignin (22%). The amounts of these biopolymers vary according to the plant and its age (Garcia-Reyes and Rangel-Mendez, 2009), e.g., Conrad and Bruun, (2007) reported a content of 7.7, 36.6,

20.6 and 35.1% for soluble compounds, cellulose, hemicellulose and lignin, respectively, in coconut

fiber, using a different extraction method. Even so, the results are similar to those reported in this

study. Regarding the results of elemental analysis, the main element present in the coconut fractions

was carbon: CcF had a slightly higher percentage (73.75%) than CsF (67.23%) and F (66.87%).

Hydrogen (6.92-7.63%) and nitrogen (9.53-10.92%) were very similar between the three materials.

Oxygen had a higher presence in CsF (15.26%) and F (14.41%), compared to CcF (6.13%). These

results took into consideration the ash percentage of 1, 1.57 and 2.15% for CsF, CcF and F,

respectively. Tsamba et al. (2006) reported a content of 53.9, 5.7, 0.1, 39.44 and 0.7% for carbon,

hydrogen, nitrogen, oxygen and ash, respectively, in coconut shell. The differences in our study

may be related to the pyrolytic method that they used.

3.3. FTIR Analysis

The results showed that the spectra obtained for the three biosorbents are similar (Fig. 1). The bands

1750 and 1660 cm^{-1} were attributed to carboxylic groups associated to aliphatic and aromatic

compounds present in hemicellulose and lignin, respectively (Garcia-Reyes and Rangel-Mendez,

2009). The analysis also suggested that the lignocellulosic residues have nitrogen-containing

functional groups (e.g. amine and amide) linked to the transmittance bands at 1590 cm^{-1}, also weak

bands at 894 and 1460 cm^{-1} were attributed to bonds C-N-O and N-H, respectively (Garcia-Reyes

and Rangel-Mendez, 2009; Velazquez-Jimenez et al., 2013); these groups can be associated with

the protein structure of the biosorbents. As explained above, the main components of the

biosorbents possess hydroxyl groups, which were confirmed by the bands around 3350 cm^{-1}

(Garcia-Reyes and Rangel-Mendez, 2009). Moreover, the band at 1030 cm^{-1} confirmed the presence

of C-O and O-H bonds that were associated with stretching vibrations of phenolic structures related

to lignin (Kushwaha et al., 2013; Velazquez-Jimenez et al., 2013). It is important to mention the

presence of overtones or combination bands in the range of 1800-2500 cm^{-1}, which were attributed

to aromatic structures related to lignin (Acheampong et al., 2011; Kushwaha et al., 2013;

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Velazquez-Jimenez et al., 2013). The CH_3 and CH_2 groups regularly exhibit characteristic bands between 2872 and 2962 cm^{-1}; these groups were associated with aromatic ring structures. Finally, stretching vibrations of carbonyl (-C=O) and carbon-oxygen single bond (-C-O), associated with hemicellulose and lignin structures (Velazquez-Jimenez et al., 2013), were located near 1750 and 1250 cm^{-1}, respectively.

3.4. Functional Group Quantification and Charge Distribution

An acid-based titration technique was implemented to determine the active sites that could participate in hydrocarbon uptake. The three principal pKa values identified were attributed to: carboxylic groups (3<pKa<5.5) present in cellulose and hemicellulose, which was confirmed by infrared spectra, nitrogen groups associated with amine-amide groups (5.2<pKa<7.2) related to the protein structure of the biosorbents, which was confirmed by ATR-FTIR, and finally phenolic groups (8<pKa<11) present in lignin structure of coconut-based biosorbents. Table 2 shows the concentration of functional groups of the materials under study.

On the other hand, the surface charge distribution of CsF and CcF was quite similar, while F showed an increase of its negative charge distribution (Fig. 2), which is related to its higher concentration of oxygenated surface groups (carboxylic and phenolic). In this case, at an approximate pH of 6.8 (CsF), 6.3 (CcF) and 5 (F), the biosorbents have a neutral surface charge. It is important to mention that the charge distribution of the biosorbents CsF and CcF in a pH range of 5-9 is close to neutral, which helps the removal of apolar compounds such as benzene, toluene and naphthalene. During the experiments, the pH of the solutions containing hydrocarbons had a value of 6 ± 0.5, therefore, the surface charge density that took the material was slightly positive for CsF and CcF, while F had basically a negative surface charge. It is known that adsorbent materials with functional basic groups promote the adsorption of organic molecules (Flores-chaparro et al., 2016;

Shukla et al., 2006). Here, the basic behavior of the biosorbents could be due to π electrons of the aromatic rings of lignin, which can favor aromatic interactions between adsorbate and adsorbent.

3.5. Adsorption Equilibrium Isotherms

As shown in Fig. 3, aromatic hydrocarbons adsorption produced two steps isotherms, i.e., isotherms in which a double layer or bilayer could be formed. The data reported for these biphasic isotherms were fitted considering a two-steps Langmuir type isotherm (Mestre et al., 2014), i.e., the Langmuir equation (Eq. 2) was fitted independently to the data of each step.

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \qquad (2)$$

where q_{max} is the maximum adsorption capacity (mg/g) and b (L/mg) the Langmuir constant related to the adsorption energy or affinity. The results reported in Table 3 show that the R^2 values are principally between 0.97 and 0.99, therefore, the Langmuir model fits correctly to the experimental data obtained in the two-steps isotherms. In addition, these adjustments allow us to know the maximum adsorption capacity for each monolayer (q_{max}).

Biphasic isotherms have been scarcely reported (Jafari Behbahani et al., 2014; Maretto et al., 2014; Mestre et al., 2014). For example, Mestre et al., (2014) studied the removal of iopamidol from aqueous solution using commercial and laboratory synthesized carbons. The isotherms obtained with the carbons synthesized in laboratory showed an adsorption isotherm in two steps, which was attributed to textural characteristics of carbons and molecular aggregation of iopamidol. In the case of the present study, it suggests that the biphasic isotherms describe that: the first adsorbed layer occurs through forces between biosorbent and adsorbate; these are intermolecular forces involving π electron rich molecules (Waters, 2002) that favor the interactions between aromatic rings of lignin and the rings of the studied compounds. The second layer depends on the adsorbate-adsorbate interactions, where aromatic interactions could also occur between the same pollutants.

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In all cases, F (Table 3) had the highest adsorption capacities followed by CcF and CsF. In general, the three biosorbents had a low porous structure, but F had a higher surface area than CsF and CcF (Table 1) and hence it is assumed that for this reason coconut fiber had the greatest adsorption capacity. Furthermore, it has been reported that the hollow tubular arrangement of F (Fig. S1-B) improves the adsorption of hydrocarbons (Wahi et al., 2013). In addition, another possibility is that the high concentration of phenolic groups in coconut fiber (F>CcF>CsF), associated to the lignin structure, enhanced the adsorption of aromatic hydrocarbons. As it is known, lignin can be the primary means of storage of organic contaminants, and so a high content of this structure can result in a high affinity for dissolved hydrocarbons (Abdolali et al., 2014; Tran et al., 2015; Wahi et al., 2013; Zhang et al., 2014).

Table S1 reports the maximum hydrocarbon adsorption capacities for different adsorbents. As it is observed, the coconut waste biosorbents have acceptable adsorption capacities of 225, 96 and 5.85 mg/g of benzene, toluene and naphthalene, respectively. It should be considered that these biosorbents did not receive any treatment and that they are abundant wastes in several countries, including Mexico. This make them low-cost materials and therefore could be revalorized as adsorbents for petroleum spills. It should be mentioned that the following studies regarding adsorption kinetics, pH and dissolved organic matter effect are only considered for coconut shell with fiber (CcF) because it is the common form as the residue can be found. In addition, the coconut shell (endocarp) provides mechanical stability to the biosorbent, which permits its packing in adsorption processes such as in permeable reactive barriers.

3.5.1. pH and Dissolved Organic Matter Effect

The working solutions were deionized water (DW) and natural water from the San Jose reservoir (NW) located in San Luis Potosi, Mexico; the latter was used to evaluate the effect of dissolved

organic matter (DOM) in the adsorption process. The DOM concentration (14 mg/L) and the main parameters found in NW are reported in Table S2.

According to the pH_{PZC} of CcF (6.3), its surface has a slight positive charge at pH 6, which can promote interaction with the π electrons of the conjugated aromatic rings of benzene, toluene, and naphthalene, which maintain a high negative density in the center of the molecule. On the other hand, CcF at pH>6.3 has a negative surface charge, and it can interact with the periphery of the aromatic rings, which have a slight positive density. However, the negative surface charge on CcF does not vary significantly in the pH range of 7 to 9 (Fig. 2). Therefore, slight changes in adsorption capacities were observed (Fig. 4).

Moreover, the adsorption capacities of benzene, toluene and naphthalene increased on average up to 47% in NW, which is associated with the effect of DOM. As it has been reported, the DOM acts as a sorbent for hydrophobic compounds such as aromatic hydrocarbons (Moon et al., 2003; Xiao et al., 2014). In this work, it is proposed that the DOM adsorbs onto the lignocellulosic biosorbent, i.e., the hydrophobic DOM sites formed by complex aromatic structures could interact with the biosorbent through π interactions, and thus increasing the concentration of adsorption sites for aromatic hydrocarbons. This is in agreement with Xiao et al., (2014) who suggested that the dissolved humic substances are accessible to the incorporation of organic compounds, and these preferentially bind to the fraction of humic acids of DOM, which represent the most aromatic fraction of the organic matter.

3.6. Adsorption Kinetics

Adsorption kinetics studies were performed in order to evaluate the time required to reach equilibrium for each contaminant (Fig. 5). This information is needed to design appropriate adsorbers (Garcia-Reyes and Rangel-Mendez, 2010). As it is shown, the time needed to reach equilibrium was approximately 5 hours, although 83, 81 and 77% of benzene, toluene and

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naphthalene, respectively, were removed in the first 90 minutes. These removal percentages are based in the maximum adsorption capacity observed in Fig. 5. The time to reach adsorption equilibrium of aromatic hydrocarbons using biosorbents reported in the literature varied, e.g. Agarry et al., (2013) reported a time of 1 h for naphthalene adsorption onto tea leaves (*Camellia sinensis*) chemically pretreated to facilitate naphthalene uptake. Xi and Chen, (2014) reported 24 and 8 h to reach adsorption equilibrium of phenanthrene and pyrene respectively, using tea leaf residues. Moreover, Younis et al., (2015) reported a time of 90 minutes for naphthalene adsorption, using rice straw (*Oryza sativa*) and sugarcane bagasse (*Saccharum officinarum*). In our study, the time for conducting the adsorption process was short and similar among the three hydrocarbons, probably because of the low porosity of CcF that minimized diffusion problems, hence it is suggested that the adsorption process took place largely on the outer surface of the material. The experimental data were fitted to the pseudo-first and pseudo-second order kinetics models, and the kinetic parameters are summarized in Table S3. The pseudo-second order model fitted better to the experimental data, based on the values of R^2, which assumes that chemisorption occurs (Garcia-Reyes and Rangel-Mendez, 2010). However, in this case this statement would not be correct. A better interpretation is that the best fit is related with the attraction forces between aromatic hydrocarbons and biosorbents, which are intermolecular forces involving π electrons interaction.

3.6.1. *Equimolar Kinetics and Dissolved Organic Matter Effect*

In order to assess the competitive adsorption between the molecules of aromatic compounds under study, equimolar adsorption kinetics were carried out. Also, the effect of the DOM in this process was evaluated. Fig. 6 shows that the time required to reach equilibrium was 5 hours for all three compounds, which coincides with the time that was obtained for the kinetics that were made individually for each compound. The adsorption capacity (Fig. 6-A) was much greater for naphthalene (9.5 µmol/g) than for toluene (3.95 µmol/g) and benzene (3.89 µmol/g).

The employed lignocellulosic biosorbents have an affinity for organic molecules associated with the presence of lignin in their structure. In this case, naphthalene was the most adsorbed compound since it is the most hydrophobic of the three compounds used, which explains its high affinity for the lignocellulosic biosorbent. Regarding toluene and benzene, their adsorption capacities were quite similar and were inhibited by the presence of a more hydrophobic molecule with higher affinity for the biosorbent. These results agree with the experimental enthalpy change ΔH_T determined in the adsorption process of benzene, toluene or naphthalene with the CcF biosorbent, where negative values confirm the exothermic nature of the adsorption process. More negative values, i.e. more exothermic, were observed for naphthalene confirming the stronger interaction forces between the adsorbent and the hydrocarbon, promoting the adsorption process over toluene and benzene (Table 4). Therefore, more hydrophobic compounds are preferably adsorbed: octanol–water partition coefficient (log K_{ow}) for naphthalene, toluene and benzene is 3.33, 2.73 and 2.13, respectively (Yang et al., 2013).

When equimolar adsorption kinetics were performed in NW (Fig. 6-B), it was observed that the time required to conduct the adsorption process was the same as for the equimolar kinetics with DW, and the adsorption capacity of aromatic hydrocarbons followed the same trend naphthalene> toluene> benzene, which also indicates that the diffusion process is negligible. Additionally, the adsorption capacity increased in NW. In this regard, although the pH of the solutions containing DOM was 7.8, this does not significantly alter the surface charge distribution of CcF. Therefore, the increase of adsorption capacities was associated with the presence of DOM, as already reported in Section 3.5.1.

3.7. Heating of Combustion of Impregnated Biosorbents

The reuse of waste is crucial in a cost-effective process. In an adsorption process the exhausted adsorbent material, when this is not regenerated, is obtained as a waste. In this sense, it is proposed

to use biomass as an environmentally safe source of energy, specifically combustion processes considerably reduce the volume of waste and produce net energy that can be used (Rambo et al., 2015; Ronda et al., 2016). In this work, the heat capacity of the CcF adsorbent, impregnated or not, was investigated (Table 4). The non-impregnated adsorbent material (control) showed 4407.79 cal/g, this value agrees with those reported in the literature for coconut residues (4469-4667 cal/g). Additionally, this is even higher than the calorific values reported for firewood from different types of trees (3400-4000 cal/g) (Musabbikhah et al., 2016; Rambo et al., 2015). Furthermore, the saturated materials with hydrocarbons showed an increment in heat capacity from 4407.79 cal/g to 4614.85, 4652.54 and 5064.43 cal/g for benzene, naphthalene, and toluene, respectively.

The calorific value of biofuels is a property influenced by the chemical composition of biomass. It has been observed that high calorific values are proportional to the amount of lignin present in the material because it has less oxygen than other cellular components (Rambo et al., 2015). Another important parameter that directly affects the calorific value is the ash content. Materials with a high ash content have a lower calorific value causing low energy yields and, at the same time, problems of maintenance and cleaning due to the accumulation of residues in the combustion chamber (Almendros et al., 2015; Lamare and Wing, 2001). In this regard, the analysis of the biosorbent materials studied in this research revealed a high content of lignin and in turn of carbon (73.75%) and low ash content (1.57%), as described in Section 3.2, which suggests coconut biomass as a promising biofuel. Moreover, the results also showed, as already mentioned, that the impregnated materials with the hydrocarbons have a higher calorific value compared to the controls (4407 up to 5064 cal/g), attributed the nature of the adsorbate-adsorbent interaction.

4. Conclusions

Through the present study, the adsorption capacity of benzene, toluene and naphthalene from water with different characteristics, by using the mesocarp and endocarp of coconut waste as biosorbents

was determined. Through the characterization of these biosorbent materials, the adsorption mechanism of hydrocarbons was established. Finally, the suitability of hydrocarbon-loaded coconut-biosorbents for energy production by combustion was investigated.

The results showed that F had the highest adsorption capacity, followed by CcF and CsF. Moreover, lignin contributes significantly to the adsorption process of aromatic compounds. Biphasic adsorption isotherms were obtained, which was attributed to the strong affinity of hydrocarbons by the same molecules initially adsorbed, these results suggest that the adsorption mechanism is governed by π-π interactions. Equilibrium and kinetics results showed that the adsorption capacity of aromatic hydrocarbons in equimolar solutions followed the trend naphthalene>toluene>benzene, and about 50% of these pollutants are removed in 90 minutes. The results indicate that the sorption of aromatic hydrocarbons onto CcF is exothermic in nature under the experimental conditions selected. It was also found that dissolved organic matter in natural water increased on averaged up to 47% the adsorption capacity of aromatic compounds onto CcF in the pH range of 6-9. Heat of combustion analysis of impregnated CcF with hydrocarbons reveled a heat capacity increase of up to 657 cal/g. Finally, this study suggests the feasibility of using coconut waste to remove soluble petroleum compounds considering that these biosorbents are available in large quantities, possess a considerable adsorption capacity and the exhausted residue, as a value-added biomass, can be used as an energy source.

Acknowledgements

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HIGHLIGHTS

- Coconut fiber (F) had the highest hydrocarbons adsorption capacity

- The materials were characterized and the adsorption mechanisms were deduced

- The effect of pH and DOM in natural water on hydrocarbons removal was determined

- HC-loaded biosorbents are a good alternative to produce energy

TABLES

Table 1

Textural properties of coconut waste fractions.

Biosorbent	Pore Volume (cm^3/g)			BET Area (m^2/g)
	Micropores	Mesopores	Macropores	
CsF	1.9×10^{-5}	7.3×10^{-4}	7.1×10^{-4}	0.40
CcF	1.5×10^{-5}	7.2×10^{-4}	8.7×10^{-4}	0.41
F	1.6×10^{-4}	9.1×10^{-4}	1.1×10^{-3}	0.75

Table 2

Functional groups concentration in coconut fractions.

Material	Carboxyl Groups (mmol/g)	Nitrogen Groups (mmol/g)	Phenolic Groups (mmol/g)
CsF	0.04	0.04	0.14
CcF	0.07	0.06	0.16
F	0.07	0.08	0.41

Table 3

Fitting parameters considering a two-steps Langmuir type isotherm.

Compound	Biosorbent		q_{max} (mg/g)	b (L/mg)	R^2
	CsF	1st step	65	0.67 x 10^{-3}	0.99
		2nd step	160	1.96 x 10^{-3}	0.99
Benzene	CcF	1st step	120	1.23 x 10^{-3}	0.97
		2nd step	175	3.90 x 10^{-3}	0.99
	F	1st step	131	1.60 x 10^{-3}	0.97
		2nd step	225	2.23 x 10^{-3}	0.99
	CsF	1st step	27	9.55 x 10^{-3}	0.99
		2nd step	43	2.66 x 10^{-3}	0.97
Toluene	CcF	1st step	42	2.65 x 10^{-3}	0.97
		2nd step	66	4.18 x 10^{-3}	0.97
	F	1st step	68.5	5.49 x 10^{-3}	0.97
		2nd step	96	2.09 x 10^{-3}	0.98
	CsF	1st step	1.6	252 x 10^{-3}	0.99
		2nd step	2.34	47.9 x 10^{-3}	0.90
Naphthalene	CcF	1st step	1	69.6 x 10^{-3}	0.98
		2nd step	2.7	34.3 x 10^{-3}	0.99
	F	1st step	3	106 x 10^{-3}	0.98
		2nd step	5.85	445 x 10^{-3}	0.99

Table 4

Enthalpy change during the adsorption of benzene, toluene and naphthalene by CcF biosorbent and heat of combustion of the impregnated biosorbents.

Treatment	ΔH_T (kcal/mol)	Heat of combustion (cal/g)
Control	-0.0041 ± 0.01	4407.79 ± 11.6
Benzene	-3.4245 ± 0.09	4614.85 ± 95.2
Toluene	-5.8608 ± 0.67	5064.43 ± 86.8
Naphthalene	-8.8149 ± 0.26	4652.54 ± 53.9

FIGURE CAPTIONS

Fig. 1. ATR-FTIR spectra of coconut shell (CsF), coconut shell with fiber (CcF) and coconut fiber (F).
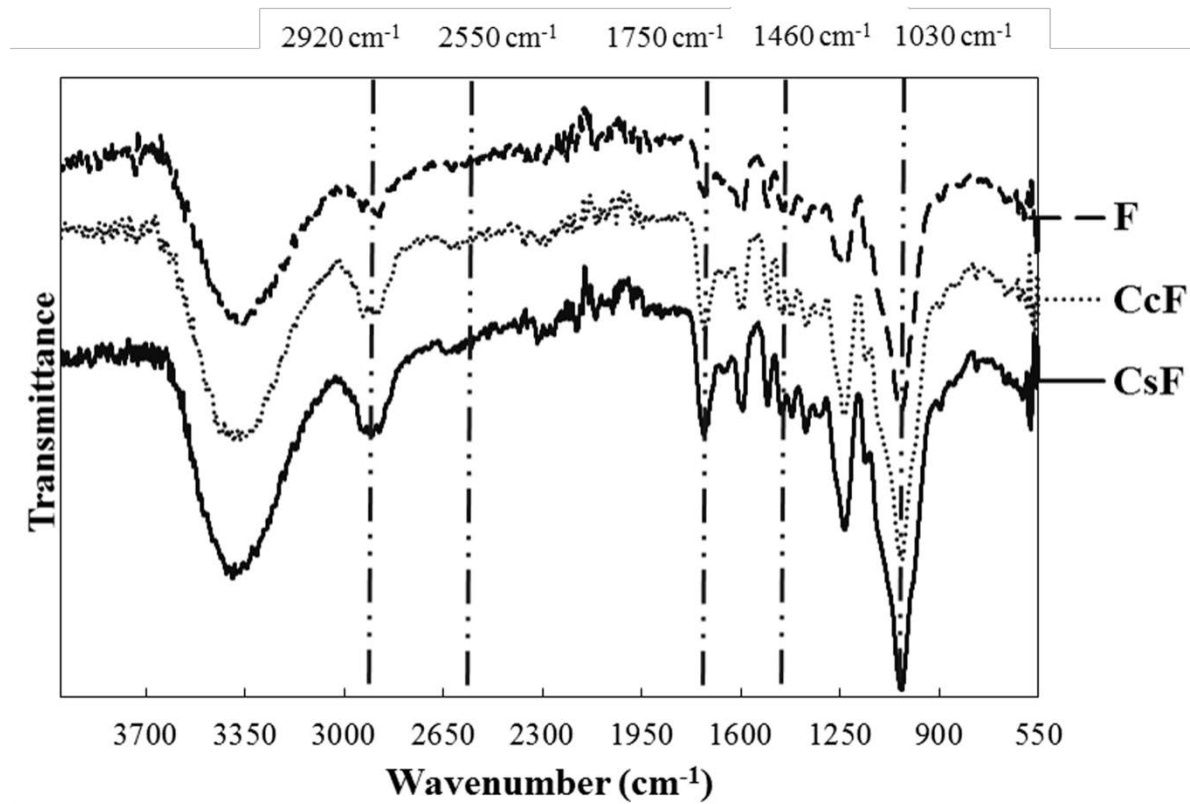
Fig. 2. Surface charge distribution of coconut shell (CsF), coconut shell with fiber (CcF) and coconut fiber (F), at an ionic strength of 0.1 N NaOH.
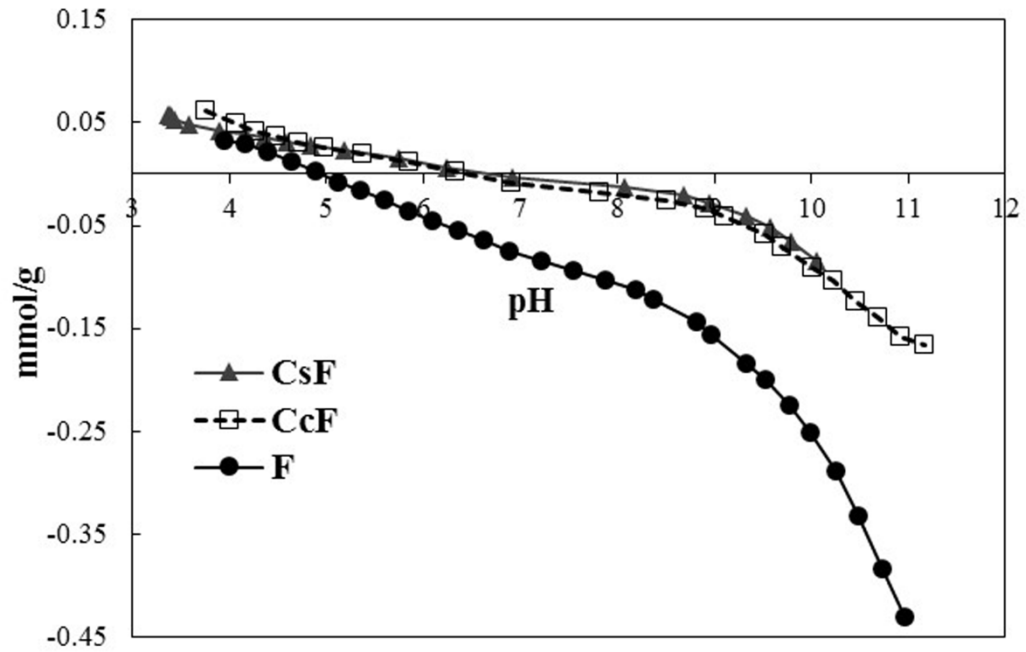
Fig. 3. Benzene (A), toluene (B) and naphthalene (C) adsorption isotherms by coconut shell (CsF), coconut shell with fiber (CcF) and coconut fiber (F) at 25 °C and initial pH of 6±0.5.
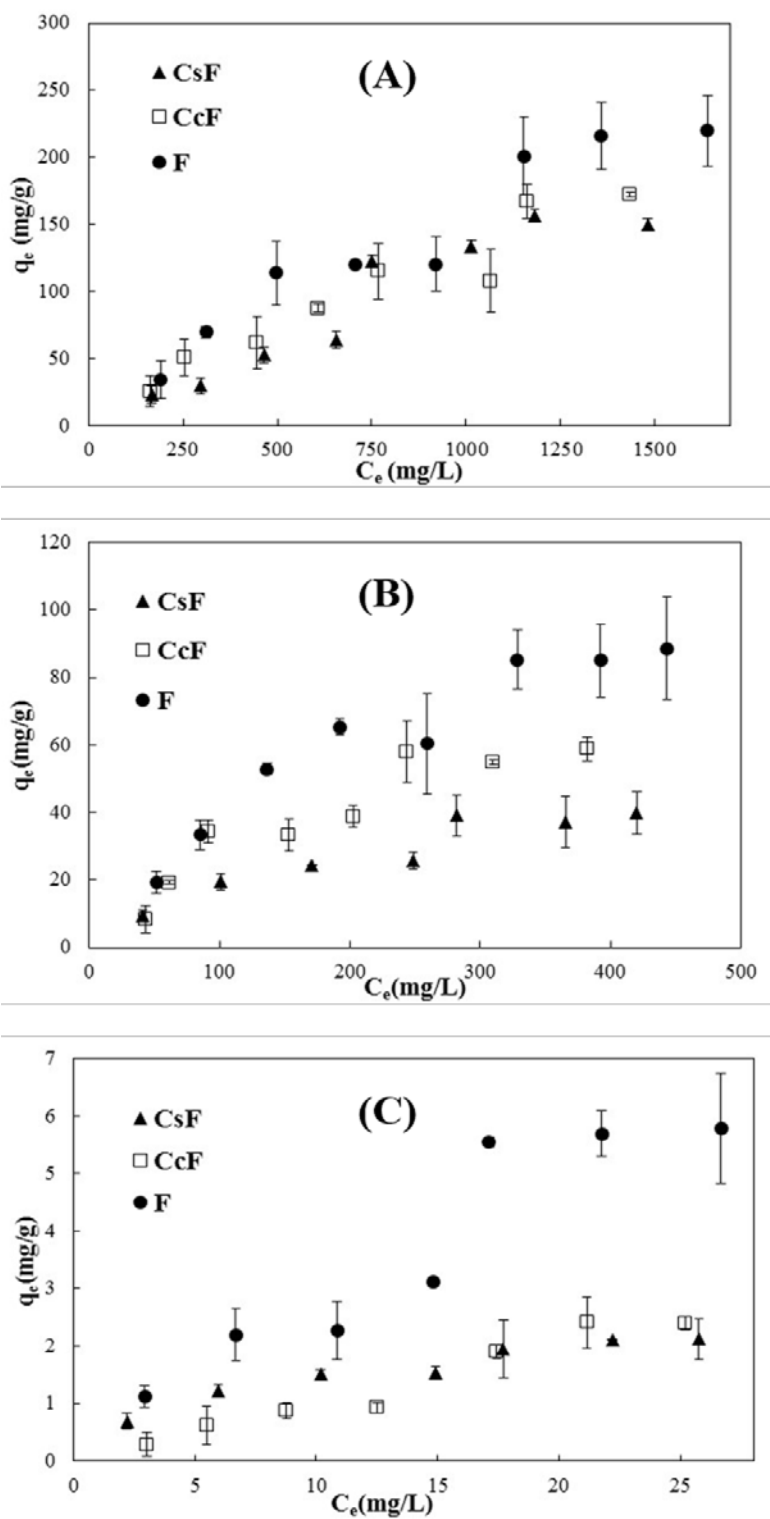
Fig. 4. pH and dissolved organic matter effect in benzene (A), toluene (B) and naphthalene (C) adsorption onto coconut shell with fiber (CcF), using deionized water (DW) and natural water (NW) at 25 °C, $C_o(A)=1500$ mg/L, $C_o(B)=500$ mg/L and $C_o(C)=30$ mg/L.
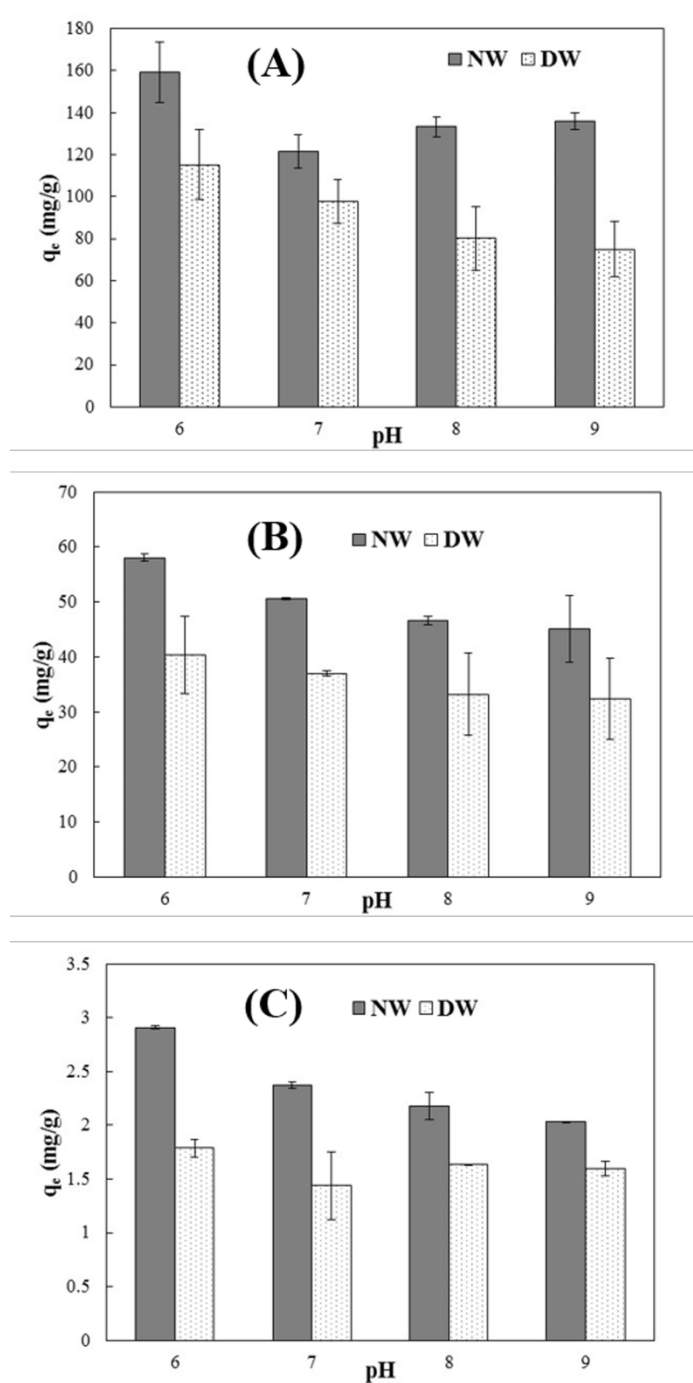
Fig. 5. Adsorption kinetics for benzene (C_o=1500 mg/L), toluene (C_o=500 mg/L) and naphthalene (C_o=26 mg/L) using coconut shell with fiber (CcF) at 25°C, 110-120 rpm and initial pH 6±0.5.
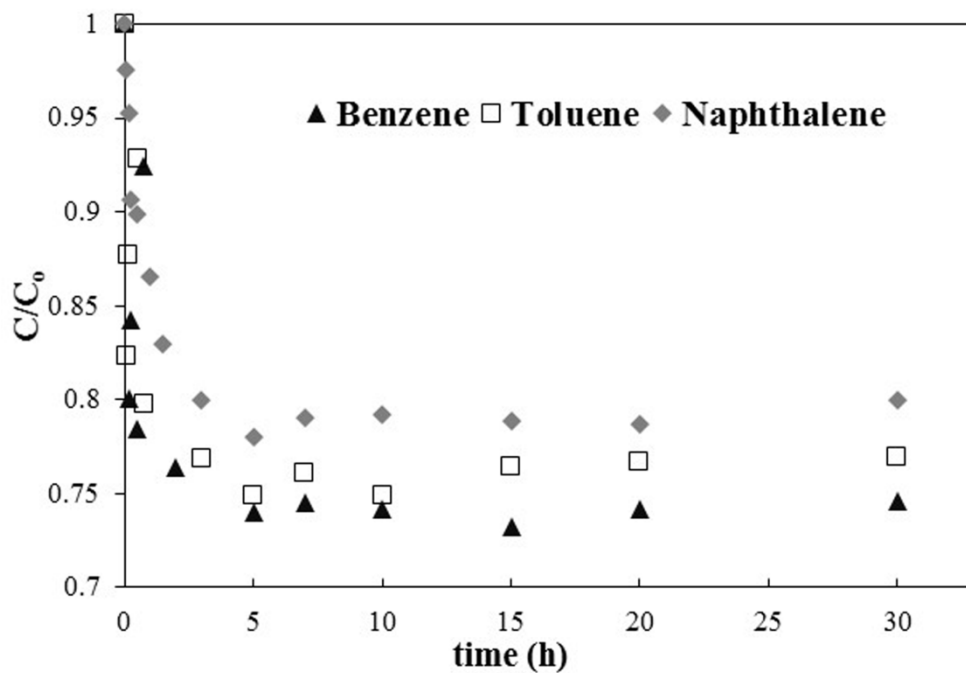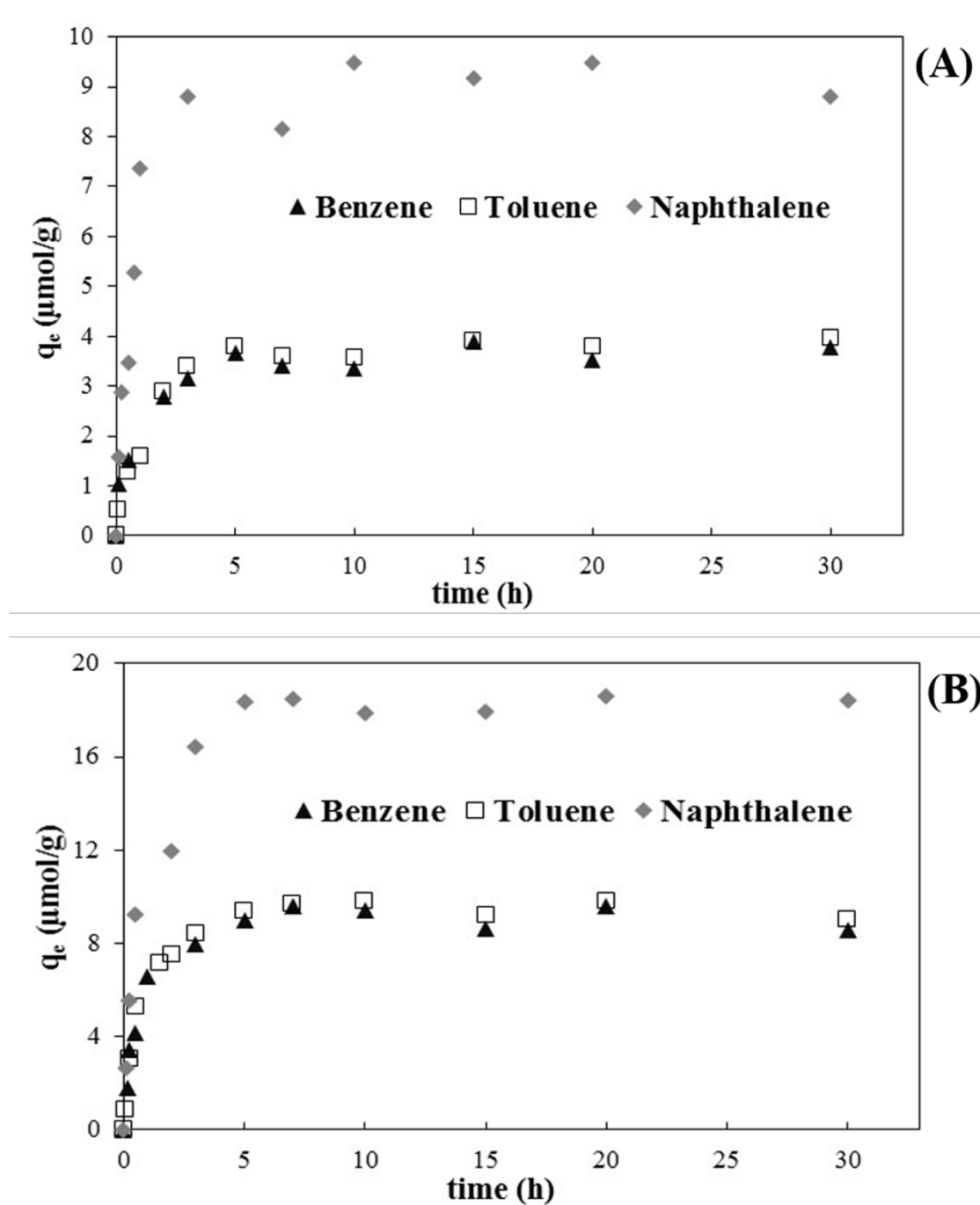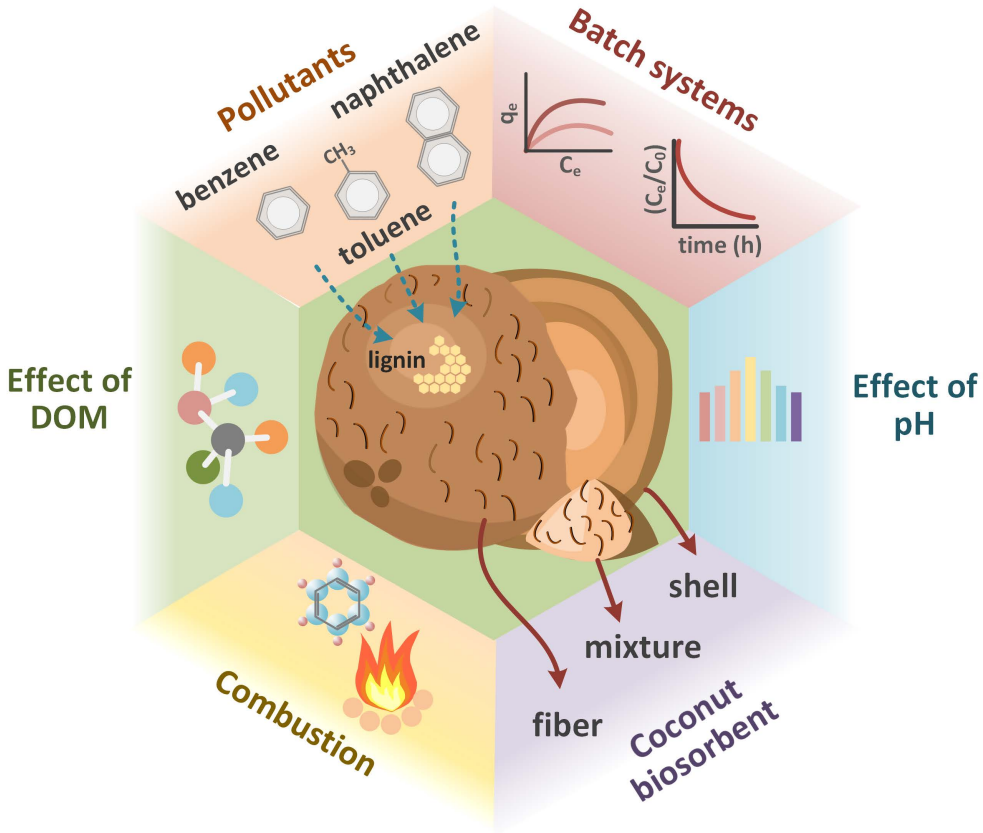
Fig. 6. Equimolar adsorption kinetics using deionized water (A) with initial pH 6±0.5 and natural water with DOM (B) with initial pH 7.8, both experiments at 25°C, 110-120 rpm and C_o=195 µmol.

Pollutants

benzene

naphthalene

CH_3

toluene

lignin

Batch systems

q_e

C_e

(C_e/C_0)

time (h)

Effect of DOM

Effect of pH

Combustion

Coconut biosorbent

shell

mixture

fiber

AQUATIC PHASE HYDROCARBONS BIOSORBENTS

BIOSORBENT-COCONUT SHELL AND HUSK RESIDUE

CONTAMINANT SOURCE - HYDROCARBONS

PERMEABLE REACTIVE BARRIER

CONTAMINATED GROUNDWATER

TREATED GROUNDWATER

SATURATED BIOSORBENT POWER SOURCE