BJEDIS Brazilian Journal of Experimental Design, Data Analysis and Inferential Statistics

Federal University of Rio de Janeiro
BJEDIS, Rio de Janeiro, v. 02 (1), 2022
DOI: https://doi.org/10.55747/bjedis.v2i1.52472
E-ISSN: 2763-6925

Received 02/10/2022. Revised 03/01/2022. Accepted 03/23/2022. Published 05/16/2022.

Solid-gas adsorption kinetics of the naphthalene on silica and XAD-2.

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Abstract: Polycyclic aromatics hydrocarbons (PAH) are an important class of pollutants ubiquitous in the environment, being spread from their source to different parts of the world and has already been related to many health issues. Its major font of production is on the burning or pyrolysis of fuels and during asphalt applications. Adsorption process has been used on-air samplers and polluted media remediation and to a better result kinetics information of the process is necessary. A system to monitor the gas → solid mass transfer was developed to represent the presence of PAH on the air. Adsorption of naphthalene in XAD-2 and silica, as separated adsorbents and as mixtures, were studied and a mixture of them in a proportion of 2:1 XAD-2/silica gave the best results in terms of the mass of PAH adsorbed and process kinetics. Improvements on the system developed have to be made for future experiments with PAH with a higher molecular weight.

Keywords: PAH, uptake, Adsorption, XAD-2, Silica.

Adherence to the BJEDIS' scope: This work reports the mathematical calculations and modeling applied in the comprehension of the heterogeneous gas-liquid transfer of naphthalene on different adsorbents.

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1. INTRODUCTION

Organic compounds that have two or more condensed aromatic cycles are called Aromatic Polycyclic Hydrocarbons (PAH) and are an important class of pollutants. These compounds, mainly formed during the burning or pyrolysis of fossil fuels and organic matter, are stable of difficult degradation and are ubiquitous in the environment, commonly found as complexes mixtures (1).

PAH and its derivatives, such as Nitro-PAH and Sulfur-PAH, are toxic and have mutagenic and carcinogenic potential for humans and other living beings, with evidence of modification on cells' gene expression, development of colon cancer and hepatic damage, influence on the modulation of drug deliver and plasmatic proteins and influence on the action of some enzymes (1-6). During pregnancy the mother's exposure to PAH is of great importance since it leads to the fetus exposure and may lead to the fetus' bad brain development, DNA damage and even abortion (7-9). Not just prenatal but also early-life exposure to PAH are related to depressed height gain of children and future behavioral problems such as attention deficit hyperactivity disorder (ADHD) (10-11).

The presence of those compounds has already been detected in the atmosphere and residential dust, water, sediments, foods and drinks, soils, petroleum, medicinal plants, breast milk and maternal and cord blood plasma (12-30). Efforts have been made to understand the transport and transformation of PAH in different media since its generation by anthropogenic activity influences not only the local region but also can spread to remote regions such as Antarctica and the Amazon Forest (31-35). PAH contamination may happen by breathing polluted air, drinking polluted liquids, smoking, or eating food that has been cultivated in contaminated soil but people who work with asphalt preparation and application are more likely to be contaminated with PAH due to their direct exposition to the asphaltic fumes, which have a high PAH content (1, 36).

Adsorption is the bonding of some particle to a surface. When this bonding occurs by van der Waals' interactions then it is called physisorption (37). When the bonding occurs with the formation of new chemical bonds then it is called chemisorption (37). Pollutant removal techniques and air samplers are commonly based on adsorption reactions and when applying the adsorption phenomenon it is necessary to have information about thermodynamic and kinetic aspects to obtain more details on the performance and mechanism, being possible to infer an equipment scale based on that information (13, 38-42).

Kinetic processes of adsorption are described with mathematical formalism such as first-order equation, pseudo-first-order equation, second-order equation, pseudo-second-order equation and Elovich's equation (43). The diffusive adsorption models take in the count or the diffusion throw a liquid film around the adsorbent's particles, or the diffusion in the liquid inside the pores of the adsorbent, or the diffusion throw the adsorbent pore walls and the sorption/desorption equilibrium into the active sites (43). Adsorptive reaction models are originated from kinetic chemical reactions and are based on the whole adsorption process (43).

Table 1. Kinetic process of adsorption description and equations

Kinetic process	Equation	Description
First-order	$\frac{dq_t}{dt} = k_{p1}(q_e - q_t)$	Described by Lagergren in 1898, it is recognized to be the first model to estimate the adsorption rate based on the adsorption capacity. This equation is known as pseudo-first-order models when based on the concentration rather than the adsorption capacity.
pseudo-first-order	$\log(q_e - q_t) = log\ q_e - \frac{k_{p1}}{2.303} t$	
Second-order	$\frac{d(P)_t}{dt} = k_{p2}[(P)_0 - (P)_t]^2$	Described in 1995 by Ho, it assumes that the limiting on the adsorptive process is the electron exchange between the adsorbent and the adsorbate. The pseudo-second-order equation is based on the concentration rather than the adsorptive capacity.
pseudo-first-order	$V_0 = k_{p2}q_e^2$	
Elovich	$q = \left(\frac{2,3}{\alpha}\right)\log\,(t + t_0) - \left(\frac{2,3}{\alpha}\right)\log t_0$	Elovich's equation has good applicability to explain de adsorption of gases into solids.

The following study aims to evaluate naphthalene (Nap), anthracene (Ant) and chrysene (Chr) with the techniques of Fluorescence Emission and Molecular Absorption on the UV-VIS length. The chosen technique will be used to measure the mass transfer phenomenon from the PAH in the gaseous phase to the solid-state adsorbents. The adsorbents used in the study are XAD-2, Silica and mixtures of XAD-2/Silica on the ratios 1:2, 1:1 and 2:1. A mass transfer analysis will be carried based on the observations made. The information obtained in this experiment is expected to be used to produce a lapel sensor for workers from the asphalt industry and even to produce an air sampler with higher sensitivity to PAH.

2. MATERIALS AND METHODS

2.1. Experimental

In the following work common laboratory glassware were used, such as beakers, volumetric flasks, volumetric pipettes and micropipettes with 10.0 – 100.0 µL and 100 – 1000 µL variable volumes (Brand). Acetonitrile HPLC/UV-VIS grade (ACN) (Tedia Company, USA) and was used as a solvent in all the experimental steps. Naphthalene and Anthracene standards were purchased from Sigma-Aldrich (Germany) and Chrysene standard was purchased from Supelco (USA). PAHs standard solutions were prepared on ACN and storage under refrigeration (253 K). The adsorbents XAD-2 and Silica were purchased from Sigma-Aldrich (Brazil. Before its use, Silica was washed with 50 mL CAN and then dried on the stove at 313 K for 6 h.

An Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer® was used on the fluorescence emission analysis. A quartz cuvette with dimensions of 3 cm x 1 cm x 1 cm (h x w x d) was used. Firstly, the compound's wavelengths of higher excitation and peaks of emission of fluorescence were determined by conducting a fluorescence 3D scan of the three compounds. After established the best combination of excitation and emission wavelengths to be monitored, a sequence of solutions with different concentrations for each compound was analyzed and then the linear work range was identified using the method proposed by De Lima Ribeiro *et al.* (43).

The compounds UV-VIS molecular absorption spectra were generated with a Hewlett-Packard 8453 Spectrophotometer to identify the wavelength that corresponds to the peak of maximum absorption. After those wavelengths were identified a sequence of solutions with different concentrations for each compound was analyzed and then the linear work range was identified using the method proposed by De Lima Ribeiro *et al*, with the absorption ranging from 0.1000 to 1.0000 (43).

For the buildup of the adsorption system were used a 50 mL glass trap within/outlines, a 5.0 cm length glass tube with 0.5 cm of inner diameter, a lapel pump, glass wool and glass pearls were used. In this system, 5.0 mg of PAH wrapped in 10.0 mg of glass wool are inserted in one end of the tube and on the other end the adsorbent is allocated. The pump's flow was set to 1.70±0.35 mL s^{-1} and with this airflow, the PAH in the glass tube is dragged in its gaseous phase throw the tube and is collected inside the trap into the 25.0 mL of acetonitrile with an initial PAH content of 200 µg L^{-1}. Measurements of the PAH's content into the acetonitrile are made every 15 seconds and the experiment lasts a total of 2 minutes.

The increasing PAH concentration in the acetonitrile, when the adsorbent is in the glass tube, is compared with the increase of the compound's concentration when there is no adsorbent in the glass tube. A lower increase rate is expected because some mass of PAH will be adsorbed. With a mass higher than 30.0 mg of adsorbent into the glass tube occurs a reduction in the airflow, so the masses of adsorbent to be tested will be 10.0 mg, 20.0 mg and 30.0 mg. Also, experiments using mixtures of XAD-2/Silica on the ratios 1:2, 1:1 and 2:1 was carried, being the total mass of adsorbent equal to 30 mg. All experiments were carried at 293 K.

2.2 Kinect Evaluation

After gathering the experimental data, the mass of PAH on the adsorbent (µg L^{-1}) and the ratio Mass on t/Mass on t_j (m_{15}/m_j) were calculated for each point, where j is the time when the measurement was made. Taking the natural logarithm of m_{15}/m_j and plotting it versus time the angular coefficient will be the first-order coefficient and from this is possible to calculate the time necessary to adsorb half of the total mass of Nap that is adsorbed on the adsorbent. (37) The difference of the calculated mass of PAH transferred to the acetonitrile in the experiment with an adsorbent to the without is the mass of PAH retained on the adsorbent, the better the adsorbent, the more mass it will retain.

3. RESULTS AND DISCUSSION

3.1. Spectrometric Characterization of PAH

The linear concentration range and the linear regression equations were obtained for Nap. Ant and Chr on both Fluorescence and UV-VIS Absorbance techniques. The linear range was established using the method proposed by De Lima Ribeiro *et al*. (43). Ant and Chr fluorescence was not monitored at the wavelength of the highest fluorescence emission due to their overlap.

Table 2. Linear ranges and linear regression equations for each PAH on both techniques

		PAH	**Linear range (µg L^{-1})**	**Equation**	**R²**
Fluorescence $\lambda_{exc} - \lambda_{em}$ (nm)	220.00 – 333.87	Nap	25 – 250	y = 0.7148x + 14.78	0.9928
	252.00 – 448.14	Ant	30 – 300	y = 1.0401x + 27.02	0.9893
	267.00 – 361.30	Chr	10 – 275	y = 0.9310x + 6.71	0.9941
UV-VIS λ_{abs} (nm)	220.00	Nap	225 – 1000	y = 0.5897x +0.0035	0.9991
	252.00	Ant	125 – 900	y = 0.9537x +0.0098	0.9996
	267.00	Chr	100 – 900	y = 0.884x +0.0031	0.9999

As expected, the fluorescence analytical curves present a lower limit of detection in comparison with those from the molecular absorption. On the other hand, on the UV-VIS Absorbance technique, the linear concentration range was higher. Also, the determination coefficient (R²) from the linear regressions on the molecular absorbance was closer to 1.0 than those from the fluorescence emission, which indicates a better fit of on the molecular absorbance. Therefore, the UV-VIS molecular absorbance technique was chosen to be used to monitor the mass transfer process.

3.1. Development of the system used to monitor the mass transfer

A batch system was developed to promote the interaction between the gaseous PAH and the solid adsorbent. The PAH would be carried from a PAH source, passing through the adsorbent and then the residual gaseous PAH would be collected in acetonitrile. The mass transfer of PAH will be carried by forced convection using a lapel pump (44).

A system with two 50 mL traps connected by a glass tube was used. The first trap was filled with 25 mL solution 200 mg L^{-1} of Nap and it would be the source of PAH, the adsorbent would be allocated into the glass tube and the residual gaseous Nap would be collected in the second trap filled with 25 mL of acetonitrile. The mass transfer using this configuration was not effective, after two hours of operation, the mass increment of Nap in the second trap solution was 10 µg.

The second system had a similar configuration, with changes on the PAH source. In this system, 0.5 mg of Nap was deposited on 20 mg of glass wool and this glass wool with Nap was allocated on the bottom of the first trap. After 45 minutes a mass increment of 13 µg of Nap was observed on the second trap solution. Trying to improve the mass transfer rate, a new system with just one trap and the glass tube was tested.

In this third system, the source of PAH (PAH deposited on 20 mg of glass wool) was accommodated at the beginning of the glass tube, the adsorbent would be accommodated on the end of the tube and the tube would be connected to the trap with acetonitrile to collect the residual gaseous PAH. The rate of mass transfer was increased, but the total experiment time was too long due to the necessary time to prepare the PAH source. To reduce the experiment total time, the PAH source was changed.

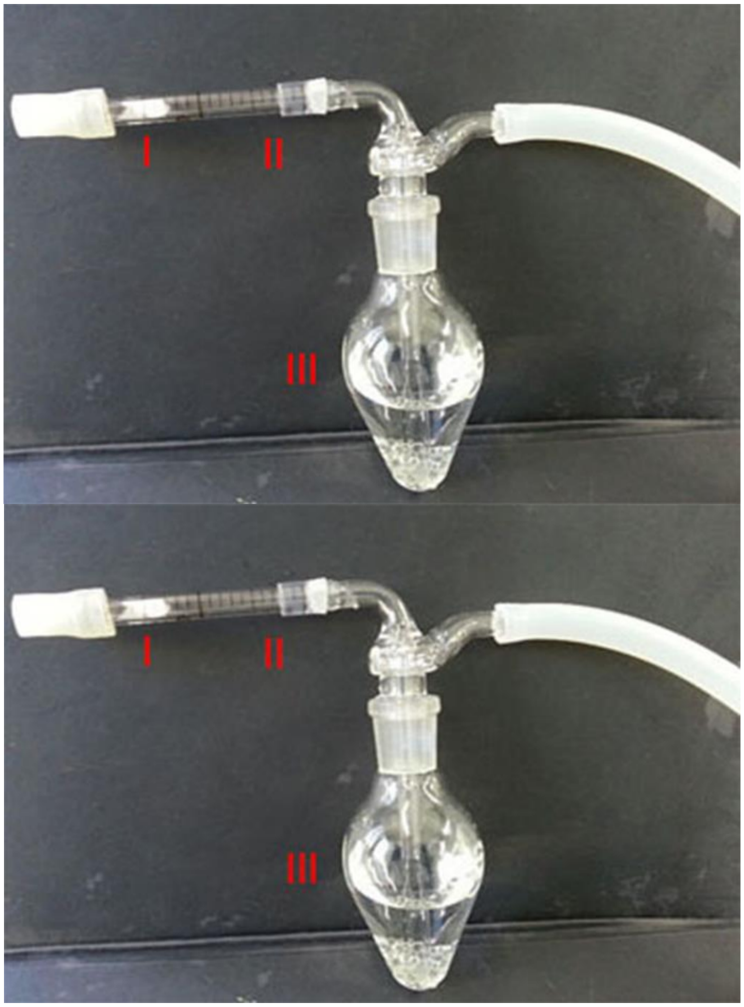

Figure 1. Glass system used to evaluate the mass transfer of PAH. There are numbered the PAH source (I), the region where the adsorbent is allocated (II) and the acetonitrile solution (III) where the residual gaseous PAH is collected.

3.2 Naphthalene mass transfer and uptake

The data gathered on the experiments with naphthalene are demonstrated below. The experiments with the separated adsorbents showed that the XAD-2 always adsorbed more Nap than Silica did when comparing the same masses of adsorbents. When used 10 mg of adsorbent, the total mass adsorbed on Silica was 26% lower than the mass adsorbed on XAD-2, 18% lower when 20 mg of adsorbent were used and 22% lower when 30 mg of adsorbent were used. This fact can be explained by the silica higher polarity due to the presence of silanol groups on its surface. Naphthalene has better interaction with XAD-2 because both are non-polar.

Table 3. Data gathered on the adsorption experiments of Nap on XAD-2 and Silica (n=3)

Adsorbent	t (s)	Mass of adsorbent					
		10 mg		20 mg		30 mg	
		ln (m_{15}/m_j)	Adsorbed PAH (μg)	ln (m_{15}/m_j)	Adsorbed PAH (μg)	ln (m_{15}/m_j)	Adsorbed PAH (μg)
XAD-2	15	–0.1968	3.14	–0.1165	3.53	–0.0243	4.17
	30	–0.3878	6.06	–0.2370	6.94	–0.0625	8.26
	45	–0.5752	8.72	–0.3662	10.32	–0.0973	12.36
	60	–0.7283	11.37	–0.4782	13.72	–0.0140	16.40
	75	–0.8201	14.17	–0.5919	16.77	–0.1696	20.52
	90	–0.9597	16.97	–0.7008	19.97	–0.1758	24.78
	105	–1.0559	19.82	–0.8032	23.30	–0.1764	28.97
	120	–1.1600	22.46	–0.9006	26.37	–0.1637	33.19
Silica	15	–0.1647	3.35	–0.0317	4.12	–0.0429	4.07
	30	–0.3824	6.11	–0.1395	7.76	–0.1279	7.90
	45	–0.6255	8.28	–0.3323	10.64	–0.2226	11.61
	60	–0.8193	10.47	–0.4899	13.60	–0.3243	15.21
	75	–0.9596	12.95	–0.6507	16.22	–0.4133	18.87
	90	–1.1116	14.98	–0.7888	18.84	–0.5139	22.34
	105	–1.2584	16.74	–0.9081	21.54	–0.5763	22.92
	120	–1.3679	18.88	–0.9976	24.45	–0.6251	29.24

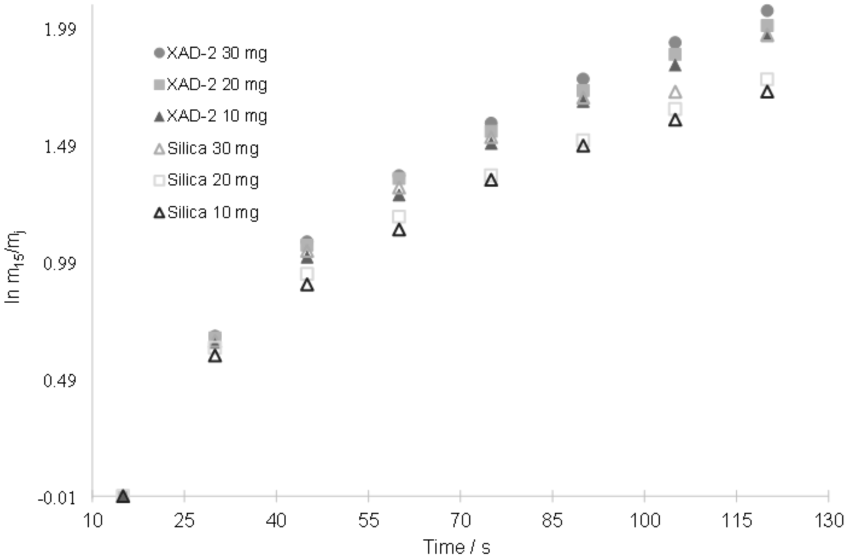

Figure 2. Plot of calculated ln (m_{15}/m_j) versus time (s) for the adsorption of Nap on different masses of both adsorbents.

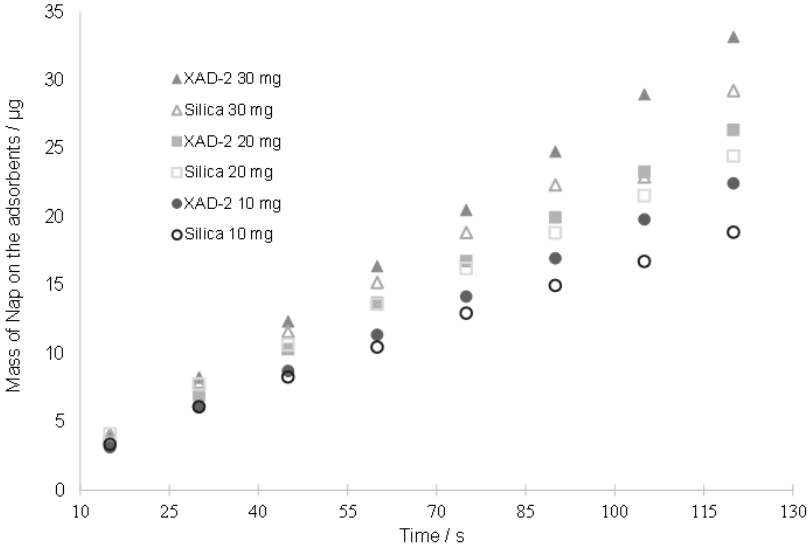

Figure 3. Increasing mass (µg) of Nap on different masses of both adsorbents over time (s).

The adsorption of Nap was also evaluated on a XAD-2/Silica mixture. In this case, the two adsorbents were used in three different proportions with a final total mass of adsorbents equal to 30 mg. When more Silica was in the mixture than XAD-2 the total amount of PAH adsorbed was 9% and 20% lower than when 30 mg of pure Silica and XAD-2, respectively, were used as adsorbents. When Silica and XAD-2 were used in the same proportion, the amount of Nap adsorbed was around 10% higher than when just Silica was used but around 5% lower than when XAD-2 was used separately. Using a higher proportion of XAD-2 than Silica the amount of Nap adsorbed was 13% higher than when Silica was used as a single adsorbent but was approximately the same amount adsorbed when just XAD-2 was used.

Table 4. Data gathered on the adsorption experiments of Nap on XAD-2/Silica mixtures (n=3)

t (s)	(XAD-2:Silica) ratio					
	1:2		1:1		2:1	
	ln (m_{15}/m_j)	Adsorbed PAH (µg)	ln (m_{15}/m_j)	Adsorbed PAH (µg)	ln (m_{15}/m_j)	Adsorbed PAH (µg)
15	–0.0768	3.85	–0.0164	4.24	–0.0231	4.18
30	–0.1458	7.69	–0.0576	8.36	–0.0472	8.34
45	–0.2102	11.49	–0.0998	12.41	–0.0809	12.45
60	–0.2798	15.18	–0.1460	16.43	–0.1018	16.62
75	–0.3367	19.00	–0.2036	20.45	–0.1392	20.69
90	–0.3827	22.85	–0.2467	24.45	–0.1642	24.83
105	–0.4368	26.64	–0.3130	28.23	–0.1822	28.92
120	–0.4845	26.75	–0.3650	32.12	–0.2043	32.97

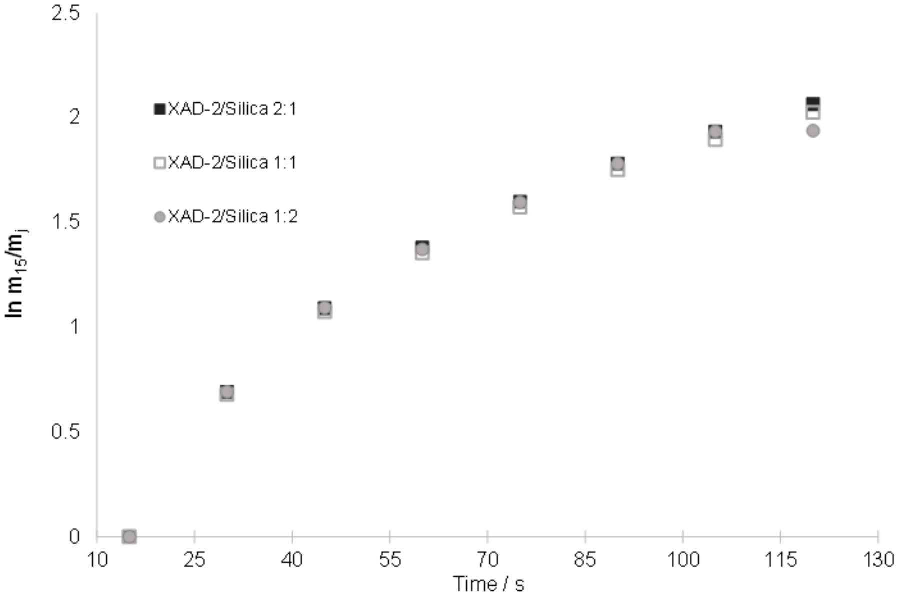

Figure 4. Plot of calculated ln (m_{15}/m_j) versus time (s) for the adsorption of Nap on different mixtures of XAD-2 and Silica within a total mass of 30 mg.

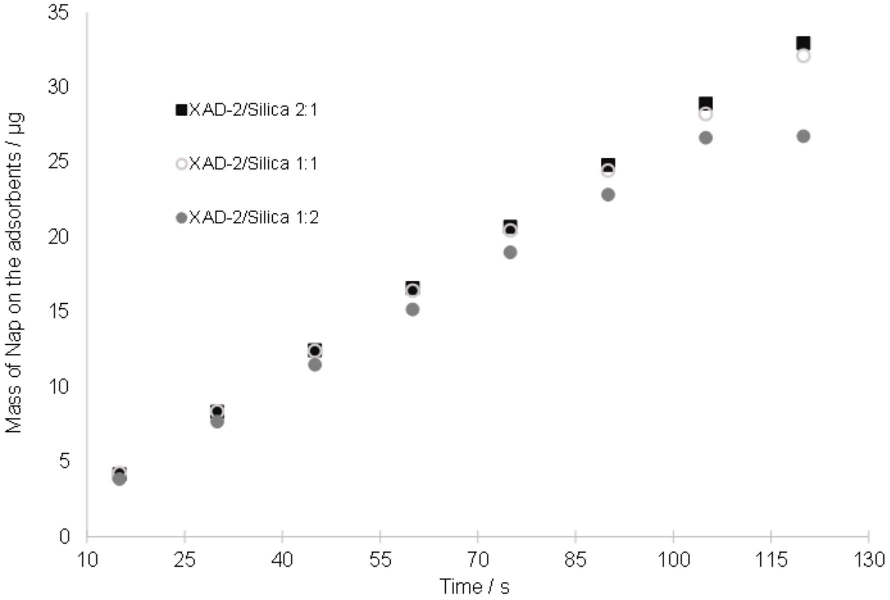

Figure 5. Increasing mass (µg) of Nap on different mixtures of XAD-2 and Silica within a total mass of 30 mg.

The higher the mass of adsorbent used, the higher becomes the first-order coefficient, which indicates a faster process of mass transfer. The first-order coefficient in the experiments, when used XAD-2, was always higher than when using Silica. As matter of fact, in the experiment in which were used 10 mg of XAD-2 the first-order coefficient was around 3% higher than when used 30 mg of Silica. Silica may present silanol groups in its surface, which gives it a higher polarity, in contrast with the surface of XAD-2, a polymer with a more nonpolar surface. Nap is a nonpolar molecule, so the intermolecular interactions of its molecules will be more efficient with nonpolar substrates, and as well its adsorption. Then the difference in the surface's polarity between the two adsorbates may explain the faster adsorption of Nap on XAD-2 rather than on Silica.

Table 5. First-order coefficient at 293 K and time to adsorb half of the total mass of PAH adsorbed on the adsorbents ($t_{1/2}$), for the experiments with XAD-2 and Silica as adsorbents (n=3)

Adsorbent	**Mass of adsorbent**					
	10 mg		**20 mg**		**30 mg**	
	First-order coefficient (s^{-1})	**$t_{1/2}$ (s)**	**First-order coefficient (s^{-1})**	**$t_{1/2}$ (s)**	**First-order coefficient (s^{-1})**	**$t_{1/2}$ (s)**
XAD-2	0.0174	39.84	0.0177	39.16	0.0183	37.88
Silica	0.0152	45.60	0.0154	45.01	0.0169	41.01

Table 6. First-order coefficient at 293 K and time to adsorb half of the total mass of PAH adsorbed on the adsorbents ($t_{1/2}$), for the experiments with XAD-2/Silica mixture as adsorbents (n=3)

(XAD-2:Silica) ratio					
1:2		**1:1**		**2:1**	
First-order coefficient (s^{-1})	**$t_{1/2}$ (s)**	**First-order coefficient/ (s^{-1})**	**$t_{1/2}$ (s)**	**First-order coefficient (s^{-1})**	**$t_{1/2}$ (s)**
0.0175	39.61	0.0179	38.72	0.0182	38.09

The experiments when used a XAD-2/Silica ratio of 1:2 presented a first-order coefficient higher than with any experiment with Silica and higher than when used 10 mg of XAD-2, but lower than on the other experiments with pure XAD-2. When used the ratio of 1:1 of XAD-2/Silica, the calculated first-order coefficient was higher than the coefficient obtained in all the other experiments where Silica and XAD-2 were used separately or in a mixture ratio of 1:2, but not higher than the coefficient calculated on the experiment in which 30 mg of XAD-2 were used. The first-order coefficient calculated when used a ratio of XAD-2/Silica of 2:1 was equal to the coefficient when used 30 mg of pure XAD-2 and higher than all other experiments.

3.3 Anthracene and Chrysene mass transfer and adsorption

When Ant and Chr were used on the system, it was not possible to observe any mass transfer. Ant and Chr have molecular weight 39% (178.23 g mol^{-1}) and 78% (228.29 g mol^{-1}) higher, respectively than Nap (128.17 g mol^{-1}).[1] Also, the Nap vapor pressure, which is 1.4 Pa, is much higher than the vapor pressure from the other compounds (2×10^{-3} Pa for Ant and 5.7×10^{-7} Pa for Chr).[1] This higher molecular weight and their even lower vapor pressure associated with a room temperature of 293 K preclude them to sublimate and then be carried by the airflow. [1]

CONCLUSION

When XAD-2 was used as a single adsorbent, with a total mass of 30 mg, presented the higher mass uptake and the higher first-order coefficient when compared with any other experiment when used XAD-2 or silica as single adsorbents on the experiments with XAD-2. The mixture of XAD-2/silica on a ratio of 2:1, for a total mass of 30 mg of adsorbents, had a higher mass uptake and a higher first-order coefficient on the experiments with XAD-2 than any other mixture of adsorbents. The values of mass uptake and first-order coefficients on the experiments with 30 mg of pure XAD-2 and 30 mg of XAD-2/silica mixture in a ratio of 2:1 is approximately the same. So, for a lapel monitor of Nap or an air sampler, it would be an economic advantage to use an XAD-2/silica mixture in a 2:1 ratio.

The system used in these experiments has to be improved to study the adsorption of heavier PAH, such as Ant and Chr. The most important factor is to add a device to make the temperature control. Heavier PAH needs a higher temperature to volatilize and without temperature control, it is not possible to achieve. Also, experiments closer to the reality during the asphalt application at higher temperatures will be needed.

CRediT author statement

Lisandro von Mulhen: Conceptualization, Methodology, Data analysis, and Writing-Original draft preparation. **Ronaldo Antunes Funari Junior:** Reviewing and Editing. **Bryan Brummelhaus de Menezes:** Supervision, Reviewing and Editing. **Lucas Mironuk Frescura:** Supervision, Reviewing. **Marcelo Barcellos da Rosa:** Conceptualization, Supervision, Reviewing and Editing.

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