

Adsorption of mercury by carbonaceous adsorbents prepared from rubber of tyre wastes

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Abstract

Rubber from tyre wastes has been used to prepare carbonaceous adsorbents and the products obtained have been tested as adsorbents for mercury in aqueous solution. The adsorbents have been prepared by applying thermal, chemical and combined (thermal and chemical or vice versa) treatments. Tyre rubber has been: heated at 400 or 900 °C for 2 h in N₂, chemically-treated with H₂SO₄, HNO₃ or H₂SO₄/HNO₃ solution for 24 h, and in two successive steps first heated at 400 °C for 2 h in N₂ and then treated with a H₂SO₄/HNO₃ solution for 24 h, or vice versa. Resultant products have been characterised in terms of elementary composition and textural properties. The adsorption of mercury has been studied from kinetic and equilibrium standpoints. The treatments effected to tyre rubber decrease the carbon content and the hydrogen content. The oxygen content and the nitrogen content increase for the chemically-treated products. The heat treatment of tyre rubber results in a larger development of surface area, microporosity, and mesoporosity than the chemical treatments. These treatments, however, produce a great creation of macropores. In comparison to the starting rubber, the adsorption process of mercury is faster when the material is heated or treated with the H₂SO₄, HNO₃ or 1:3 H₂SO₄/HNO₃ solution. These adsorbents are either a non-porous solid or possess a high mesopore volume or a wide pore size distribution in the macropore range. The adsorption capacity is larger for products prepared by heat, chemical and combined treatments of the rubber. A common textural characteristic of these adsorbents is their better developed microporosity. The ability to adsorb mercury is higher for the heated products than for the chemically-treated ones. The maximum adsorption of mercury is 211 mg g⁻¹. The constant K_f of the Freundlich equation is as high as 108.9 mg g⁻¹.

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1. Introduction

More of 330 million waste tyres are discarded each year [1]. Ground tyres can be used in civil engineering applications, for example as an additive in road pavement [2]. Other applications include in playground surface [3], rubber roofs [4], drainage systems [5], and floor mats [6]. A major market for scrap tyres is their utilisation as solid fuels [7], especially

in cement kilns [8]. These applications of the tyre rubber do not appear to be sufficiently profitable as tyres are frequently dumped in the open, becoming a serious source of environmental pollution.

Because the carbon content is high in tyres, i.e., 70–75 wt.% for cars and 68–72 wt.% for lorries [9], a good solution for recycling tyre waste is likely to convert them to valuable products such as carbonaceous adsorbents. These are very extensively used in the adsorption of organic and inorganic solutes from aqueous solution [10]. The properties of an adsorbent that are important to adsorption processes

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depend on the starting material and on the method used in their preparation. Accordingly, the use of inexpensive materials such as wastes with such an aim will certainly lower the production cost of the adsorbent. At present, in fact, low-cost adsorbents are being frequently tested for heavy metal removal from contaminated water [11].

The World Health Organization (WHO) reported that between 25,000 and 125,000 tons of mercury were released into the environment in 1976 [12]. Mercury is regarded as one of the most harmful metals found in the environment [13,14]. Hence, its removal from wastewaters, before these being discharged into the environment, is necessary. Recently, the use of activated carbon [15–20], elemental carbon particles [21], silica-dithizone [22], functionalised sol–gels [23], and carbon aerogel [24] to remove mercury from aqueous solution has been investigated. Tyre rubber has also been used with such an aim [13,25] and for the immobilisation of mercury(II) in contaminated soil [26]. On the other hand, the production of active carbons from waste tyres has been reviewed [27]. The results obtained in a previous study of preparation of carbonaceous materials from waste tyre rubber by applying thermal, chemical and combined methods and of textural characterisation of the resultant products have been reported [28]. Here, the samples are tested as adsorbents of mercury from aqueous solution. The adsorption process is studied from both kinetic and equilibrium standpoints. Specifically, the influence of properties of the adsorbent as the composition and texture (i.e., surface area, pore volumes and pore size distribution) on such respects of the adsorption process is investigated.

2. Experimental

2.1. Material

The starting material used in this study was size-reduced residual rubber (RR, hereafter) obtained from tyre wastes. The material (average particle size between 1 and 3 mm) was supplied by the Escuela Politécnica Superior de Alcoy (Alicante, Spain).

2.2. Preparation of adsorbents

In the heat treatments of RR, a vertical cylindrical furnace (Chesa) and a stainless steel reactor were used. Approximately, 10 g of rubber was weighed and heated at 400 or 900 °C for 2 h in N₂ (flow rate = 225 ml min⁻¹). The heating rate was 10 °C min⁻¹. In the chemical treatments of RR, however, 25 g of the material, 125 ml of distilled water, and 125 ml of acid solution (i.e., the water/acid ratio used was 1:1 by volume) were added to a glass flask. The acid solution was commercial H₂SO₄ or HNO₃ or a mixture of these acids at three H₂SO₄/HNO₃ ratios by volume. The system was allowed to react for 24 h. In the combined treatments, RR was first heated at 400 °C for 2 h in N₂ (flow rate = 225 ml min⁻¹) and then chemically-treated with a H₂SO₄/HNO₃ solution,

Table 1
Preparation of carbonaceous adsorbents from RR

Treatment	Temperature (°C)/acid solution	Notations
Heat	400	H-400
Heat	900	H-900
Acid	H ₂ SO ₄	C-S
Acid	HNO ₃	C-N
Acid	H ₂ SO ₄ /HNO ₃ (75%/25%)	C-S/N (3:1)
Acid	H ₂ SO ₄ /HNO ₃ (50%/50%)	C-S/N (1:1)
Chemical	H ₂ SO ₄ /HNO ₃ (25%/75%)	C-S/N (1:3)
Heat/chemical	400-H ₂ SO ₄ /HNO ₃ (25%/75%)	HC-400-S/N (1:3)
Chemical/heat	H ₂ SO ₄ /HNO ₃ (25%/75%)-400	CH-S/N (1:3)-400

and also vice versa. The H₂SO₄/HNO₃ ratios used in the chemical treatments of RR and the notations of the samples can be seen in Table 1.

2.3. Elemental chemical analysis

The elemental analysis of RR and the carbonaceous adsorbents prepared from it was determined in the Instituto Nacional del Carbon y sus Derivados (C.S.I.C., Oviedo, Spain), using a LECO micro-analyser. This was made up of both VTF-900 and CHNS-932 determination units with suitable detectors. Data of such an analysis are collected in Table 2.

2.4. Textural characterisation

The textural characterisation of the samples was accomplished by gas adsorption (N₂, -196 °C), mercury porosimetry, and helium and mercury density measurements, as reported before [28]. The values of textural parameters (i.e., specific surface area and pore volumes) are set out in Table 3.

2.5. Adsorption of mercury

Mercuric chloride of reagent grade, as supplied by Probus, was used in the preparation of the adsorptive solutions. In the kinetic experiments, approximately 0.08 g of sample was first placed in a suit of test tubes provided with Bakelite screw-up caps. Then, 25 ml of a stock 4 × 10⁻³ M HgCl₂ aqueous solution were added. Next, the tubes were placed in a Selecta thermostatic shakerbath, containing water at 25 °C. The liquid and solid phases were maintained under continuous agitation of 50 oscillations min⁻¹ a different time ranging between 5 min and 360 h. By this experimental procedure,

Table 2
Data of the elemental analysis (wt.%) of RR and selected samples

Sample	C	H	N	S	O
RR	83.52	7.28	0.33	0.02	3.08
H-400	71.63	0.94	0.25		7.21
H-900	74.29	0.75	0.18	0.08	2.75
C-S/N (3:1)	68.24	3.84	2.93		13.85
C-S/N (1:3)	69.89	2.28	3.15		11.24
HC-400-S/N (1:3)	78.43	1.05	0.70	0.06	6.10
CH-S/N (1:3)-400	73.79	1.81	3.20		7.69

Table 3
Textural data for the samples^a

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	W_0 ($\text{cm}^3 \text{g}^{-1}$)	V_{me} ($\text{cm}^3 \text{g}^{-1}$)	V_{ma} ($\text{cm}^3 \text{g}^{-1}$)	V_{T} ($\text{cm}^3 \text{g}^{-1}$)
RR	0.0	0.001	0.04	0.03	0.08
H-400	18.1	0.043	0.40	0.21	0.77
H-900	47.4	0.045	0.34	0.31	0.82
C-S	2.3	0.001	0.03	0.06	0.15
C-N	2.0	0.005	0.08	0.56	0.80
C-S/N (3:1)	5.7	0.012	0.13	0.52	0.84
C-S/N (1:1)	5.0	0.010	0.09	0.57	0.85
C-S/N (1:3)	7.5	0.041	0.07	0.69	1.02
HC-400-S/N (1:3)	14.0	0.050	0.24	0.24	0.94
CH-S/N (1:3)-400	5.0	0.010	0.07	0.61	0.92

^a N_2 isotherms at -196°C : S_{BET} (specific surface area, BET equation, $p/p^0 = 0.05-0.35$, $a_m = 16.2 \text{ \AA}^2$), W_0 (micropore volume, Dubinin–Radushkevich equation). Mercury porosimetry: V_{me} (mesopore volume), V_{ma} (macropore volume). Density measurements: V_{T} (total pore volume) = $1/\rho_{\text{Hg}} - 1/\rho_{\text{He}}$, ρ_{He} = helium density and ρ_{Hg} = mercury density.

apparent adsorption rates were determined. The adsorption isotherms were measured using between 0.01 and 0.25 g of sample. An aliquot of 25 ml of the 4×10^{-3} M solution was added to each glass tube. The adsorption system was kept under contact until equilibration was reached, which as a rule took less than 100 h.

After contact of the HgCl_2 solution with the adsorbent, the supernatant liquid was filtered and analysed by UV–vis spectrometry, using a Shimadzu equipment. The analytical method was set up by first investigating the volume of commercial HCl that ought to be added to a HgCl_2 solution to assure the total conversion of HgCl_2 to $\text{Cl}_4\text{Hg}^{2-}$, which is the complex anion formed by reaction between HgCl_2 and HCl in aqueous solution. This study enabled one to fix not only such a volume but also the wavelength of maximum absorption of the HgCl_2 solution, which proved to be 230 nm. At this wavelength value, the absorbance of a set of adsorptive solutions was then measured as a function of concentration to know if the absorbance–concentration data obeyed the Lambert–Beer’s law well [29].

To get an insight into the pH change caused in the adsorptive solution as result of the adsorption process, the pH of the 4×10^{-3} M HgCl_2 solution was measured after 7 days, both on this solution itself and on the resultant residual liquid after contact of 25 ml of such a solution with approximately 0.12 g of each adsorbent.

3. Results and discussion

3.1. Elementary analysis

From data of the chemical analysis of the samples (Table 2) it follows that the heat and chemical treatments of RR cause important changes in the chemical composition of the material. As a result, the carbon content and the hydrogen content significantly decrease. Furthermore, the nitrogen content decreases for H-400 and H-900, and the oxygen content also for H-900. However, the contents of nitrogen and oxygen greatly increase in C–S/N (3:1) and C–S/N (1:3). Moreover,

the sulphur content is almost negligible in the analysed samples (notice that sulphur was not amenable to the analysis for a number of them), in spite of the fact that sulphuric acid has been used in the chemical treatments of RR. These results indicate that when RR is treated with $\text{H}_2\text{SO}_4/\text{HNO}_3$ solution the nitration process prevails over the sulphonation one.

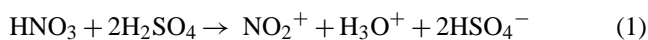
The method of preparation of the samples markedly influences the elementary composition. Thus, the carbon content is noticeably lower for C–S/N (3:1) and C–S/N (1:3) than for H-400 and H-900, whereas the contents of hydrogen, nitrogen, and oxygen are much higher for the former products. For HC-400-S/N (1:3) and CH-S/N (1:3)-400 the carbon content is also higher and the contents of hydrogen, nitrogen, and oxygen are usually lower than for C–S/N (3:1) and C–S/N (1:3). Finally, the carbon content is even higher for HC-400-S/N (1:3) than for H-400 and H-900. Because the contents of hydrogen and nitrogen are also significantly higher for HC-400-S/N (1:3) than for H-400 it appears that, after heating RR at 400°C , the remaining organic fraction concentrates in the final product owing to the removal of inorganic components from the intermediate one by action of the $\text{H}_2\text{S}_4/\text{HNO}_3$ solution. It is also supported by the somewhat lower oxygen content for HC-400-S/N (1:3) than for H-400. On the other hand, the values of the oxygen content for C–S/N (1:3) and CH-S/N (1:3)-400 suggest that oxygen complexes are mainly affected when the previously chemically-treated product is heated at 400°C . However, the nitrogen complexes must be thermally stable as the nitrogen content is similar for both samples.

As expected, the rise in temperature between 400 and 900°C in the preparation of H-400 and H-900 results in an increase in the carbon content and in a decrease in the contents of hydrogen and nitrogen and, in particular, of oxygen. The decrease in these chemical elements at 900°C agrees with the somewhat lower yield value obtained for H-400 than for H-900 (i.e., 35.0 and 33.0, respectively) [28]. It should be also noted that the oxygen content suffers an important increase for H-400 as compared to RR and a significant decrease for H-900 with regard to H-400. On the other hand, the proportion of H_2SO_4 and HNO_3 in the acid solution mainly

affects the contents of hydrogen and oxygen in the samples. Such contents are lower in C–S/N (1:3) than in C–S/N (3:1). The comparison of the composition data for the couples of samples H-400 and HC-400-S/N (1:3), and C–S/N (1:3) and CH-S/N (1:3)-400 shows the same trends as those described before for the products prepared by the single treatments of RR. They demonstrate that the predominant effect in the combined treatments of RR on the elementary composition is the one effected first.

The above-mentioned composition changes can be accounted for as follows. The heat treatments of RR result in the release of volatile matter, and consequently in mass loss. Depending on the chemical composition of the products evolved, it will be affected the relative amounts of the analysed elements in the final products. Nevertheless, the deposition of carbon may also occur, in particular at 900 °C. In earlier studies of tyre pyrolysis [30–32] it has been found that the resultant quantity of char exceeds the amount of carbon black present in the original tyres. Accordingly, the solid product was regarded as a mixture of carbon black and char formed by tyre rubber degradation.

The chemical treatments of RR with the HNO₃/H₂SO₄ solutions may produce not only mass loss by, e.g., solution of a RR component such as zinc oxide, which behaves as an amphoteric metallic oxide, but also mass increase by formation of surface complexes in the carbonaceous material of RR. Sulphuric acid, which is a strong dehydrating agent, may also cause carbonisation of organic components of RR, this leading to an increased carbon content. In aqueous solution, nitric acid combines with sulphuric acid according to



The stoichiometry of reaction (1) suggests that the formation of the nitronium ion first, and hence the nitration of the carbonaceous material of RR, is favoured when the acid solution containing a higher content of sulphuric acid is used. Only in such an instance, by action of the sulphuric acid in excess, the introduction of sulphonic groups in the carbonaceous material would be also possible. Furthermore, it would be propitiated by the fact that the reaction medium heated during the treatment of RR with the acid solution as reaction (1) is an exothermic process. However, from the low sulphur content in the chemically-treated products it becomes clear that sulphur surface complexes are not formed, to a significant extent at least. The opposite holds for the nitrogen surface complexes.

3.2. Textural characterisation

The starting material (see data in Table 3) is practically a non-porous material, V_T being equal to 0.08 cm³ g⁻¹ for RR. Furthermore, its extremely reduced porosity is made up of almost exclusively large pores, i.e., mesopores and macropores. Because W_0 is very low in RR, $S_{\text{BET}} = 0.0 \text{ m}^2 \text{ g}^{-1}$.

The single stage-heat and chemical treatments of RR as a rule develop the surface area and porosity in the resultant products. For H-400 and H-900 S_{BET} , W_0 , and V_{me} increase. V_{me} is as high as 0.40 and 0.34 cm³ g⁻¹ for H-400 and H-900, respectively. For the chemically-treated samples, as an exception, W_0 is also higher for C–S/N (1:3). However, V_{ma} greatly increases in C–N, C–S/N (3:1), C–S/N (1:1), and C–S/N (1:3). The highest value of V_{ma} (0.69 cm³ g⁻¹) appears for C–S/N (1:3). In contrast, C–S possesses a very poor development of the porosity in all ranges of pore sizes. In fact, V_T is equal to 0.15 cm³ g⁻¹ for this sample, which is similar to that for C–S. The values of the pore volumes obtained for the chemically-treated products in a single stage reveal that the creation of macropores is favoured with increasing content of nitric acid in the HNO₃/H₂SO₄ solution. However, a high concentration of sulphuric acid in such a solution mitigates the development of the microporosity. The presence of mesopores is of little significance, regardless of the composition of the acid solution.

As far as the combined treatments of RR is concerned, the effect of the chemical or heat treatment of the previously heated or chemically-treated product on the porosity depends on the range of pore sizes. For comparison purposes one can use H-400 for HC-400-S/N (1:3) and C–S/N (1:3) for CH-S/N (1:3)-400. Data in Table 3 show that the subsequent chemical treatment of H-400 causes an increase in W_0 and V_{ma} and a decrease in V_{me} . However, the heat treatment of C–S/N (1:3) produces a decrease in W_0 and V_{ma} , V_{me} remaining unchanged. As a final comment it should be noted that for the carbonaceous adsorbents prepared in this study, excluding C–S, V_T varies between 0.77 cm³ g⁻¹ for H-400 and 1.02 cm³ g⁻¹ for C–S/N (1:3). Therefore, C–S/N (1:3) possesses the best-developed total porosity.

The values of W_0 indicate that the creation of micropores as a result of the heat and chemical treatments of RR is of little significance. It holds even for H-400, H-900, C–S/N (1:3), and HC-400-S/N (1:3), in spite of the greater increase produced in the micropore volume for this series of samples. However, the mesoporosity for H-400, H-900, and HC-400-S/N (1:3) and the macroporosity for most of the samples develop to a large extent. As a guide, for different activated carbons, which are usually regarded as typical microporous solids, the volume of micropores lies between 0.15 and 0.50 cm³ g⁻¹. The volume of mesopores ranges usually between 0.02 and 0.10 cm³ g⁻¹ and the volume of macropores between 0.20 and 0.80 cm³ g⁻¹ [33].

3.3. Adsorption of mercury

3.3.1. Kinetics

Fig. 1 shows the plots of the amount of mercury adsorbed per unit mass of adsorbent (X (mg g⁻¹)) against contact time (t (h)) (X was estimated from the amounts of mercury present in the adsorptive solution before and after its contact with the adsorbent). From the X – t data the first-order adsorption rate constant (k (h⁻¹)) was estimated by applying expression (2),

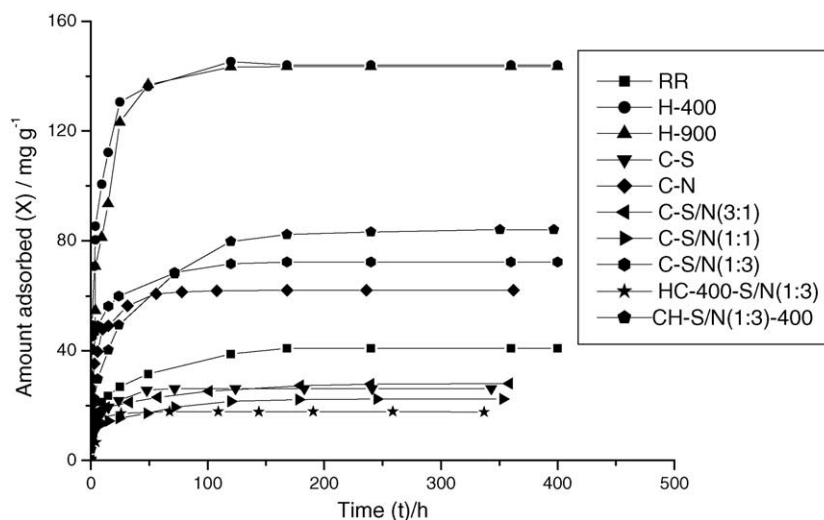


Fig. 1. Variation of the amount of mercury adsorbed with time.

which was early proposed by Lagergren [34]:

$$\log_{10}(X_e - X) = \log_{10} X_e - kt/2.303 \quad (2)$$

where X_e is the amount of metallic ion adsorbed at equilibrium per adsorbent mass unit (mg g^{-1}). It was derived in a kinetic model based on the assumption that chemisorption is the rate limiting step. The values thus obtained of r (i.e., the linear correlation coefficient) and k are listed in Table 4. The high r values obtained for all the adsorption systems denote that the $X-t$ data fit quite well to Eq. (2). Good correlation coefficients indicate that Lagergren's equation is applicable and the adsorption process is first-order [35].

As shown in Table 4, k varies in the sequence $\text{C-S} > \text{C-N} > \text{H-900} > \text{H-400} > \text{C-S/N (1:3)} > \text{RR} > \text{C-S/N (1:1)} > \text{CH-S/N (1:3)-400} > \text{C-S/N (3:1)} > \text{HC-400-S/N (1:3)}$. In comparison to RR, therefore, the adsorption process of mercury is faster for the samples prepared by heat treatment of RR at 400 or 900 °C and using the H_2SO_4 , HNO_3 or 1:3 $\text{H}_2\text{SO}_4/\text{HNO}_3$ solution in the chemical treatment of RR. In contrast, the process is slower when using the $\text{H}_2\text{SO}_4/\text{HNO}_3$ solutions containing a high H_2SO_4 content and also when RR is successively heated and chemically-treated, or vice versa. In the combined treatments of RR, the unfavourable effect of the second treatment on the

adsorption kinetics of mercury is stronger for the chemical one. In fact, the lowest value of k ($2.7 \times 10^{-2} \text{ h}^{-1}$) obtained in this study appears for HC-400-S/N (1:3).

The kinetics of the adsorption process of solutes from aqueous solution on porous solids are influenced not only by the surface functional groups of the adsorbent but also by its pore size distribution, which is the factor that controls the facility of access of the adsorptive in aqueous solution to surface active sites of the adsorbent. The mesoporosity, in particular, may play an important role in connection with the adsorption kinetics from the liquid phase. In accordance with these statements it is clear that the simple existence of a qualitative correlation between part of the elemental composition of the adsorbent, alone, and k values does not necessary imply a mechanistic significance. In any event the values of the oxygen content (wt.%) and k (h^{-1}) (Table 2) for H-400 (7.21, 3.5) and H-900 (2.75, 3.9), on the one side, and for C-S/N (3:1) (13.85, 2.6×10^{-1}) and C-S/N (1:3) (11.24, 3.1), on the other side, seem to indicate that a high content of oxygen decelerates the adsorption process of mercury. However, such values are 6.10 and 2.7×10^{-2} for HC-400-S/N (1:3) and 7.69 and 1.7 for CH-S/N (1:3)-400.

Data in Tables 3 and 4 show that the kinetics of the adsorption process of mercury are more rapidly provided that the adsorbent is a non-porous solid (RR and C-S) or the corresponding V_{me} is high (H-400, H-900). An exception to the rule is C-S/N (1:3) as for this sample, in spite of its so low V_{me} of $0.07 \text{ cm}^3 \text{ g}^{-1}$, k is somewhat higher than for RR. The speeding up of the process could be associated with a great development of the macroporosity as V_{ma} is as high as $0.69 \text{ cm}^3 \text{ g}^{-1}$ for C-S/N (1:3). However, it would be then striking the fact that for C-S/N (3:1) and C-S/N (1:1) V_{ma} (see Table 3) is also high and k presents a small value, in particular for C-S/N (3:1). Moreover, the kinetic results and the macropore volumes are rather similar for C-N and C-S/N (1:3). In view of these results it was thought that the pore size distribution in the macropore range could be the determinant

Table 4
Values of the adsorption rate constant

Sample	$k \times 10^2$ (h^{-1})	r
RR	2.1	0.9996
H-400	3.5	0.9999
H-900	3.9	0.9972
C-S	6.8	0.9959
C-N	5.0	0.9917
C-S/N (3:1)	2.6×10^{-1}	0.9971
C-S/N (1:1)	1.8	0.9980
C-S/N (1:3)	3.1	0.9998
HC-400-S/N (1:3)	2.7×10^{-2}	0.9962
CH-S/N (1:3)-400	1.7	0.9996

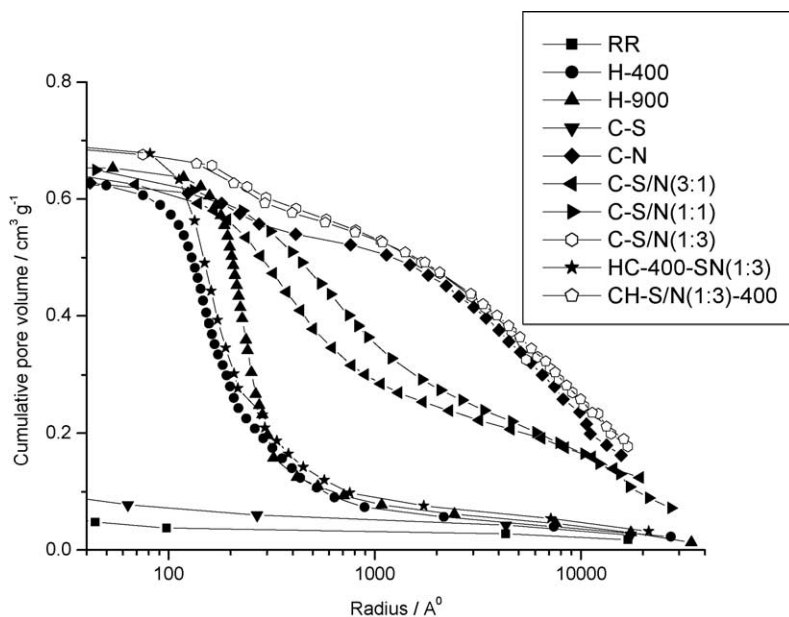


Fig. 2. Pore size distribution of the adsorbents.

factor in connection with the adsorption kinetics of mercury for the chemically-treated samples. In order to verify it the cumulative pore volume, as obtained by mercury porosimetry, has been plotted against pore radius in Fig. 2. It is seen that the pore size distribution in such a porosity region is much wider for C–N and C–S/N (1:3) than for C–S/N (3:1) and C–S/N (1:1) and that, at the same time, it is similar for the samples of each individual couple. These results suggest that the factor that greatly influences the adsorption kinetics is the pore size distribution in the macropore range, instead of the macropore volume.

The porosity of H-400 and H-900 (Fig. 2) in the meso and macropore ranges is made up of narrower pores than for most simply chemically-treated products and, however, the adsorption process is faster for H-400 and H-900 than for

C–S/N (3:1), C–S/N (1:1), and C–S/N (1:3). This indicates that the pore size that controls the adsorption kinetics of mercury depends on the method of preparation of the adsorbent. When applying chemical methods, the diffusion of the adsorptive solution in pores of the adsorbent must be hindered and as a result the presence of wider pores is needed in the material so that the adsorptive can reach surface active sites located in pore walls.

3.3.2. Adsorption isotherms

The adsorption isotherms measured for the various systems are shown in Fig. 3. The isotherms obtained for H-400 and H-900 belong to the type H2 of the system of classification put forward by Giles et al. [36] for organic solutes. The isotherms for H-400 and H-900 display a first ascending

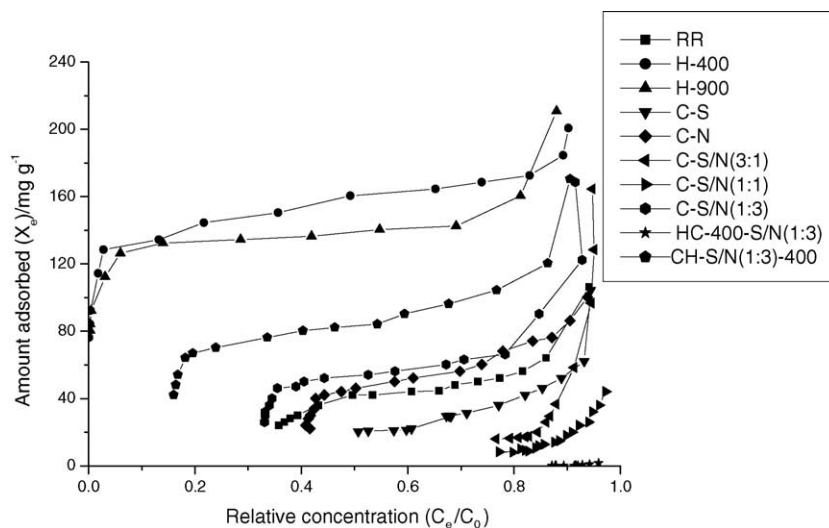


Fig. 3. Adsorption isotherms of mercury.

branch of great slope which denotes that the solute has such affinity for the adsorbent that in dilute solutions it is completely adsorbed, or at least there is no measurable amount remaining in solution. The isotherms also show a long plateau which is almost parallel to the abscissa axis and that extends practically in the whole range of C_e/C_0 values, C_e and C_0 being the equilibrium concentration and the initial concentration of the adsorptive solution. The length of this plateau was earlier associated with the energy barrier that has to be overcome before additional adsorption can continue on new active sites, after the surface has been saturated to the first degree [36]. A second rise in the isotherm was attributed to the development of a fresh surface on which adsorption can occur [36]. Such a surface may be: (a) the exposed parts of the layer already present; (b) new regions of the substrate structure into which the solute begins to penetrate; or (c) part of the original surface that may become uncovered by re-orientation of the molecules already adsorbed.

A peculiar feature of the isotherms obtained for the samples other than H-400 and H-900 is that they start defining at C_e/C_0 values that are far above $C_e/C_0 \approx 0.0$. For C-S/N (3:1), C-S/N (1:1), and HC-400-S/N (1:3), in particular, such C_e/C_0 values are around 0.8. Furthermore, for HC-400-S/N (1:3) the adsorption of mercury is very low, practically zero, over the whole C_e/C_0 range. These results denote a low affinity of the adsorbent towards the adsorptive. Also, the adsorptive-adsorbent interactions are not strong enough so that the adsorption can occur. The fact that the pH of the adsorptive solution (see Table 5) as a rule increases after a significantly long contact time with the adsorbent suggests that the adsorption process is not of ionic exchange between Hg^{2+} ions and H^+ ions since, otherwise, the pH should decrease with regard to 4.1, which is the pH of the adsorptive solution. According to the literature [37], the solubility of $HgCl_2$ in water is 6.6 g $HgCl_2/100$ g water at 20 °C. In water, most of the compound in solution is present as undissociated $HgCl_2$ molecules; a small amount dissociates, and for the equilibrium $HgCl_2 = HgCl^+ + Cl^-$, $\log K$ is about -6.55; small amounts of $HgCl_3^-$ and very small amounts of Hg^{2+} and $HgCl_4^{2-}$ are also present. Then, of these mercury species that presumably participate in the adsorption process, molecular $HgCl_2$ appears to be the most important one. It is consistent with the higher adsorption of mercury for both simply heated samples, which must be more hydrophobic adsorbents, than for the chemically-treated

ones. These products should possess a more hydrophilic character owing to the formation of nitrogen surface groups as a result of the treatments of RR with acid solutions.

The Freundlich Eq. (3) [38]

$$X_e = K_f C_e^{(1/n)} \quad (3)$$

was applied to the adsorption isotherms. Here, X_e is also the amount adsorbed ($mg\ g^{-1}$) at equilibrium. K_f ($mg\ g^{-1}$) and n are two constants which incorporate all factors affecting the adsorption process, such as adsorption capacity of the adsorbent (K_f) and the variation of the adsorption with concentration ($1/n$). The values of r , K_f and n are listed in Table 6. It is seen that K_f is as high as 108.9 $mg\ g^{-1}$ for H-900. For adsorbents prepared from various sources, values of K_f of 50.11 [16], 28.8 [18], 4.52 [19], 42.6 [20], and 6.18 [22] have been reported previously.

The values of K_f show that the adsorption of mercury is low for RR, which is in line with the poor development of surface area and porosity in this product. For the whole series of adsorbents prepared from RR K_f varies in the sequence H-900 > H-400 > CH-S/N (1:3)-400 > C-S/N (1:3) > RR > C-N > C-S > C-S/N (1:1) > C-S/N (3:1) > HC-400-S/N (1:3). The adsorption capacity, in particular, is higher for H-400 and H-900 than for RR. It is also greater for CH-400-S/N (1:3). Finally, the increase in K_f is less significant for C-S/N (1:3). Accordingly, the adsorption of mercury can be favoured by heat, chemical and combined treatments of RR. In the chemical and combined treatments, however, it is so only when in the preparation of the samples the H_2SO_4/HNO_3 solution with the highest concentration of HNO_3 is used and when the heat treatment is effected second, after the chemical treatment, respectively. In brief, heating and the greatest presence of HNO_3 in the H_2SO_4/HNO_3 solution increase the adsorption of mercury. In contrast, the adsorption is small when the acid solution used in the treatment of RR possesses a high content of H_2SO_4 and when RR is successively heated and chemically-treated.

The chemical composition of the adsorbents does not appear to be a significant factor in connection with their adsorption capacity. For example, the contents of nitrogen and oxygen (Table 2) are higher for C-S/N (1:3) than for H-900, and the amount of mercury adsorbed is however greater for

Table 5
pH change in the adsorptive solution^a

Sample	pH	Sample	pH
RR	6.1	C-S/N (3:1)	4.9
H-400	5.8	C-S/N (1:1)	4.3
H-900	7.0	C-S/N (1:3)	5.3
C-S	3.8	HC-400-S/N (1:3)	5.2
C-N	4.0	CH-S/N (1:3)-400	5.1

^a The pH of the adsorptive solution was 4.1 and remained practically constant after 7 days.

Table 6
Parameters of the Freundlich equation

Sample	K_f ($mg\ g^{-1}$)	n	r
RR	1.8	1.3	0.9987
H-400	89.1	9.8	0.9996
H-900	108.9	21.74	0.9930
C-S	1.6×10^{-4}	0.5	0.9940
C-N	0.4	1.1	0.9930
C-S/N (3:1)	2×10^{-32}	0.08	0.9977
C-S/N (1:1)	1.6×10^{-20}	1.3×10^{-1}	0.9944
C-S/N (1:3)	5.0	2.3	0.9997
HC-400-S/N (1:3)	2.3×10^{-92}	0.03	0.9982
CH-S/N (1:3)-400	17.0	3.3	0.9997

the latter product. In contrast, the micropore content in the RR-derived products seems to play a more decisive role on the extent of adsorption of mercury, in spite of the low development of the microporosity in the adsorbents. Thus, most samples with an increased adsorption capacity with regard to RR possess a higher micropore volume. For H-400, H-900, and C-S/N (1:3), in addition, K_f increases with increasing V_{mi} . An exception to the rule is however the pair HC-400-S/N (1:3) and CH-S/N (1:3)-400 as K_f is higher for the product with a lower micropore content.

4. Conclusions

- As a result of the treatments of tyre rubber, important changes occur in its chemical composition. Usually, the carbon content and the hydrogen content suffer an important decrease, whereas the nitrogen content and the oxygen content increase. Sulphur is not detected in a number of the analysed samples.
- Tyre rubber may be regarded as a non-porous material. The heat treatments of the rubber mainly develop the microporosity and, in particular, the mesoporosity. The mesopore volume may become even higher than for a typical adsorbent of solutes in aqueous solution such as activated carbon. The chemical treatments, instead, give rise to the creation of macropores. In the combined treatments, the predominant effects on the porous structure are the ones associated with the treatment effected first.
- In comparison to the starting rubber, the adsorption process of mercury is faster for the samples prepared by treatment of the material with the H_2SO_4 , HNO_3 or 1:3 H_2SO_4/HNO_3 solution and also for both heated products. The remaining chemical and combined treatments have an unfavourable effect on adsorption kinetics.
- The adsorption capacity of tyre rubber towards mercury is greatly enhanced when it is heated at 400 or 900 °C. Although less, it also increases when the material is successively chemically- and heat-treated. The favourable effect on the adsorption of mercury is still weaker when the 1:3 H_2SO_4/HNO_3 solution is used. The other treatments of the rubber lower the adsorption of mercury in comparison to the starting rubber.
- The adsorption process of mercury is faster provided that the adsorbent is a non-porous solid, its mesopore volume is high or its pore size distribution in the macropore region is wide. Usually, the adsorption capacity is larger for the adsorbents with higher developments of the microporosity.

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