Adsorption (2008) 14: 591–600
DOI 10.1007/s10450-008-9115-z

Uptake of lead by carbonaceous adsorbents developed from tire rubber

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Received: 27 April 2007 / Revised: 25 February 2008 / Accepted: 4 March 2008 / Published online: 28 March 2008

Abstract The adsorption of lead in aqueous solution by discarded tire rubber (TR) and by carbonaceous adsorbents (CAs) prepared from it by thermal and chemical treatments is studied. TR was heated at 400 or 900 °C for 2 h in N_2 atmosphere or treated chemically with H_2SO_4, HNO_3, H_2SO_4/HNO_3, HCl, NaOH, HCl-NaOH or NaOH-HCl for 24 h. TR and CAs were characterized physico-chemically with regard to their texture, elemental composition and surface chemistry. The adsorption of lead was studied, mainly from the kinetic standpoint, using 4×10^{-3} mol L^{-1} Pb^{2+} solutions at initial pH 2.0, 5.7 and 12.6. TR is practically a non-porous material. The heat treatment of TR mainly develops meso- and macroporosity. The effect on macroporosity is stronger when HNO_3 and H_2SO_4/HNO_3 are used. For all adsorbents, the adsorption of lead is not measurable when adsorptive solution at pH 2 is used. With an increase of pH from 5.7 to 12.6, the kinetics of adsorption becomes faster and the amount of lead adsorbed significantly increases. For the solution at pH 12.6 and an adsorption time of 8 h, the adsorption percentage is 36 wt% for TR. For the CAs prepared by heat treatment of TR, it is higher than 50 wt%. For longer adsorption times, the kinetics is much slower for the product of TR treatment with HNO_3. However, the corresponding adsorption percentage is as high as 93 wt% for an adsorption time of 264 h. TR and the CAs, in particular the product heated at 400 °C, are good adsorbents to be used in the rapid removal of a significant amount of lead from aqueous solution.

Keywords Tire rubber · Carbonaceous adsorbents · Lead adsorption

1 Introduction

During the last few decades, industry has had a great environmental impact. Either directly or indirectly, it has been partially responsible for the global warming, ozone depletion, soil sterilization, air contamination, pollution of water resources, etc. Nowadays, not only the specialized scientific and technical communities and the international institutions but also the general public are fully aware of the negative impact of industrial activity on the population health. As a result, new technologies are expected to be cheap, flexible, environmentally friendly and to eliminate several classes of industrial wastes. The most popular processes for the decontamination of industrial effluents are neutralization/precipitation, ion exchange, activated charcoal adsorption, separation by membrane, electrolysis, electro-reduction, electro-dialysis and biological (denitrification or nitrification of effluents) (Castells 2000). However, the complexity of treating the different polluting streams (i.e., solid/liquid and gases) generated by the different industrial sectors as well as the cost of such treatments push the scientific and technical communities to envisage new approaches.

Heavy metals are toxic to aquatic flora and fauna even in relatively low concentrations. They are capable of being assimilated, stored and concentrated by human body, causing

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nausea, diarrhoea, muscular cramps, erythrocyte destruction, renal degradation, chronic pulmonary problems, and so on (Mohan and Singh 2002). Specifically, lead is an almost ubiquitous pollutant. The lead levels in natural water are at the microgram per cubic decimeter level (O'Neill 1993). This fact is a matter of current concern as lead is a highly toxic heavy metal, its poisoning effects being cumulative. Usually, lead affects the gastrointestinal track, nervous system and sometimes both. Lead is used in storage batteries, insecticides, plastics, glasses, ceramics, paintings, water pipes, foods, beverages, ointments, and medicinal concoctions for flavoring and sweetening.

Nowadays more than 5 million tons per year of used tire are generated (De Marco Rodriguez et al. 2001). Since the carbon black content in tire rubber reaches 22 wt%, being only surpassed by that of hydrocarbon (45–48 wt%) (San Miguel et al. 2003), and its carbon content is as high as 68–75 wt%, the reutilization of this waste as starting material in the preparation of carbonaceous adsorbents was viewed before as a feasible alternative for its revalorization. Bearing these facts in mind, various carbonaceous adsorbents were obtained from tire rubber by using thermal and chemical methods (Manchón-Vizuete et al. 2004) and resultant products were tested as adsorbents of mercury in aqueous solutions (Manchón-Vizuete et al. 2005). Using a series of such carbonaceous adsorbents and also fresh products, the primary objective of the present study is to investigate the influence of the heat/chemical method of preparation of the adsorbent on its behavior in the adsorption process of lead in aqueous solution. Previously, only tire rubber (Netzer et al. 1974; Rowley et al. 1984) and carbon adsorbents prepared by thermal treatment of the material (Zhang et al. 2004; Yan et al. 2006) have been used in the adsorption of such a metallic ion.

2 Experimental

2.1 Starting material and reactants

The starting material used in this study was size-reduced TR. The material (average particle size between 1 and 3 mm) was supplied by the Escuela Politécnica Superior de Alcoy (Alicante, Spain) and, as received, used in these investigations. Commercial sulfuric acid (96 wt%, 1.835 g cm^{-3}; Carlo Erba), nitric acid (65 wt%, 1.395 g cm^{-3}; Carlo Erba), hydrochloric acid (37 wt%, 1.19 g cm^{-3}; Panreac, PRS), and sodium hydroxide pellet (98 wt%, Panreac, PRS) were used in the chemical treatments of TR.

2.2 Preparation and characterization of adsorbents

In the preparation of the CAs, TR was subjected to heat and chemical treatments. Details of the methods used were given in a previous report (Manchón-Vizuete et al. 2004). Accordingly, ∼ 10 g of TR were placed in a stainless steel reactor and heated to 400 or 900 °C in N_2 (flow rate = 225 mL min^{-1}), using a vertical cylindrical furnace. The heating rate was 10 °C min^{-1}. The isothermal time at maximum heat treatment temperature was 2 h. Moreover, ∼ 25 g of TR, 125 mL of distilled water and 125 mL of commercial H_2SO_4, HNO_3 or both mineral acids were added to a glass flask and the system was allowed to react for 24 h. The textural characterization of TR and the CAs was accomplished by gas adsorption (N_2, −196 °C), mercury porosimetry, and density measurements (Manchón-Vizuete et al. 2004). For TR and a few selected CAs the elemental analysis was also determined (Manchón-Vizuete et al. 2005). Also, the FT-IR spectra were registered. Using a spectrometer, Perkin-Elmer 1720, the spectra were recorded in the range of wave numbers 4000–450 cm^{-1}. 50 scans were taken at 2 cm^{-1} resolution. Pellets were prepared at the TR/CA to KBr impregnation ratio 1:1900. The spectrum of a KBr pellet with the same amount of dispersant as for the CA/Br pellets was used as background.

Here, four CAs were prepared by treating TR (∼ 25 g) with an aqueous solution of either HCl (125 mL of distilled water plus 125 mL of commercial product) or NaOH (250 mL, 5 mol L^{-1} NaOH solution) and successively with these HCl and NaOH solutions, and *vice versa*. Although the isotherms for N_2 at −196 °C were also determined for these four CAs, the amounts adsorbed were not measurable at low relative pressures and hence textural parameters such as the BET surface area and micropore volume could not be calculated. The methods used in the preparation of the selected CAs are summarized in Table 1. This table also lists textural data obtained for such CAs together with their notations.

2.3 Experiments of lead adsorption

Adsorptive solutions were prepared using $PbCl_2$ (Carlo Erba, RPE). In the adsorption experiments such solutions were used at unadjusted pH (i.e. ∼ 5.7) or after adding HCl or NaOH solution up to pH 2.0 or 12.6 was attained. At pH 12.6 the precipitation of insoluble species was not observed at all in the Pb^{2+} solution. Instead, as shown by the speciation diagram for the Pb^{2+} hydrolysis products (Baes and Mesmer 1976), at such a high pH value the predominant specie in a 10^{-5} mol L^{-1} Pb^{2+} solution is $Pb(OH)_3^-$. Adsorption tests were carried out using a thermostatic shaker bath (Selecta) containing water at 25 °C. Using a suit of 25 mL glass test tubes, ∼ 0.1 g of adsorbent and 25 mL of 4×10^{-3} mol L^{-1} Pb^{2+} aqueous solution were added. Accordingly, the adsorption system contained 1 mmol of Pb^{2+} per gram of CA. The liquid and solid phases were maintained under continuous agitation of 50 oscillations min^{-1} for different times ranging from 15 min to 360 h. This time was usually high enough so that equilibration was reached in the adsorption system. Determinations of lead in the residual liquid after a given adsorption time were carried out by atomic absorption spectrometry, using a Thermo Electron instrument fitted with a suitable lamp for lead analysis.

3 Results and discussion

3.1 Characterization of carbonaceous adsorbents

The values of S_{BET} and pore volumes (Table 1) indicate that TR is practically a non-porous material, its total pore volume (i.e., $W_0 + V_{\mathrm{me\text{-}P}} + V_{\mathrm{ma}}$) being as low as 0.071 $\mathrm{cm^3\,g^{-1}}$. The BET surface area is $\sim 0.0\ \mathrm{m^2\,g^{-1}}$ for TR. It follows also that the heat treatment of TR develops the porosity in the regions of micro-, meso- and macropores, the effect being stronger on meso- and macroporosity than on microporosity. Because of the creation of micropores, S_{BET} is significantly larger for T-400 and T-900 than for TR. $V_{\mathrm{me\text{-}P}}$ is 0.40 $\mathrm{cm^3\,g^{-1}}$ for H-400 and 0.34 $\mathrm{cm^3\,g^{-1}}$ for H-900. Therefore, these CAs are more mesoporous materials than a commonly used adsorbent such as activated carbon (i.e. an essentially microporous solid) for which the volume of mesopores ranges usually between 0.02 and 0.10 $\mathrm{cm^3\,g^{-1}}$ (Cookson 1978).

The chemical treatments of TR with HNO_3 and with the H_2SO_4/HNO_3 mixtures produce a great increase in V_{ma}. The V_{ma} values obtained for the resultant products, which vary between 0.52 and 0.57 $\mathrm{cm^3\,g^{-1}}$, are about twofold larger than for H-400 and H-900. For typical activated carbons the macropore volume ranges usually between 0.2 and 0.80 $\mathrm{cm^3\,g^{-1}}$ (Cookson 1978). Such chemical treatments of TR also develop microporosity in the material, though to a much lesser extent than for the heat treatments as the volume of micropores is much lower in C-N, C-S/N(3:1) and C-S/N(1:1) than in T-400 and T-900. The rest of the CAs possess a poorly developed porosity. In brief, using TR and thermal and chemical treatments-based methods, CAs with high meso- and macropore contents and with lower micropore contents are prepared.

Data of the elemental analysis obtained for TR and for a few selected CAs (Manchón-Vizuete et al. 2005) indicate that the thermal and chemical treatments of TR result in a significant decrease in the carbon and hydrogen contents. The nitrogen content decreases for the heat-treated products, whereas it increases significantly for the H_2SO_4/HNO_3-treated products. Because the oxygen content greatly increases for C-S/N(3:1) and the sulfur content is very low (i.e. it was not amenable in fact to the analysis) in this product, nitrogen surface groups likely formed as a result of the treatment of TR with the H_2SO_4/HNO_3 mixture. This statement is supported by the FT-IR spectrum registered for C-S/N(3:1) (Fig. 1), which shows a strong band at 1550 $\mathrm{cm^{-1}}$ that is ascribable to ν(N=O) vibrations in C–NO_2 atomic groupings attached to aromatic carbon atoms (Pretsch et al. 1980). The spectrum of TR displays a large number of well defined peaks which are attributable to ν(C–H), ν(C=C), ν(O–H), ν(C=O), ν(C–O), and so on vibrations. In the spectrum of C-N, as compared to the spectrum of TR, the band at 1592 $\mathrm{cm^{-1}}$ decreases noticeably in intensity with respect to the band at 1622 $\mathrm{cm^{-1}}$ and the bands located at wave numbers close to 3000 $\mathrm{cm^{-1}}$ and at 1462 and 1422 $\mathrm{cm^{-1}}$ are significantly weaker, whereas the bands at 1120 and 1039 $\mathrm{cm^{-1}}$ are stronger. These spectral changes indicate that the chemical treatment of TR with the HNO_3 solution markedly affects the surface chemistry of this material, which is worth mentioning.

3.2 Lead adsorption

The results obtained in the study of the kinetics of the adsorption process of lead in aqueous solution indicate that it is strongly dependent on pH of the adsorptive solution. When the solution at pH 2.0 is used, the adsorption of Pb^{2+} is not measurable for TR and all CAs. This is likely due to a strong competition effect between the hydrated proton, H_3O^+, and the Pb^{2+} ion for the surface active sites of the adsorbents. In fact, H_3O^+ in aqueous solution is a more mobile ion than the metal ions (Greenwood and Earnshaw 1984). Furthermore, the concentration of H_3O^+ in the Pb^{2+} solution is

Table 1 Preparation of carbonaceous adsorbents from TR. Textural data

Sample	Treatment	T (°C)/Acid/Base	S_{BET} ($\mathrm{m^2\,g^{-1}}$)	W_0 ($\mathrm{cm^3\,g^{-1}}$)	$V_{\mathrm{me\text{-}P}}$ ($\mathrm{cm^3\,g^{-1}}$)	V_{ma} ($\mathrm{cm^3\,g^{-1}}$)
TR			0.0	0.001	0.04	0.03
H-400	Heat	400	18.1	0.043	0.40	0.21
H-900	Heat	900	47.4	0.045	0.34	0.31
C-S	Acid	H_2SO_4	2.3	0.001	0.03	0.06
C-N	Acid	HNO_3	2.0	0.005	0.08	0.56
C-S/N(3:1)	Acid	H_2SO_4/HNO_3 (75%/25%)	5.7	0.012	0.13	0.52
C-S/N(1:1)	Acid	H_2SO_4/HNO_3 (50%/50%)	5.0	0.010	0.09	0.57

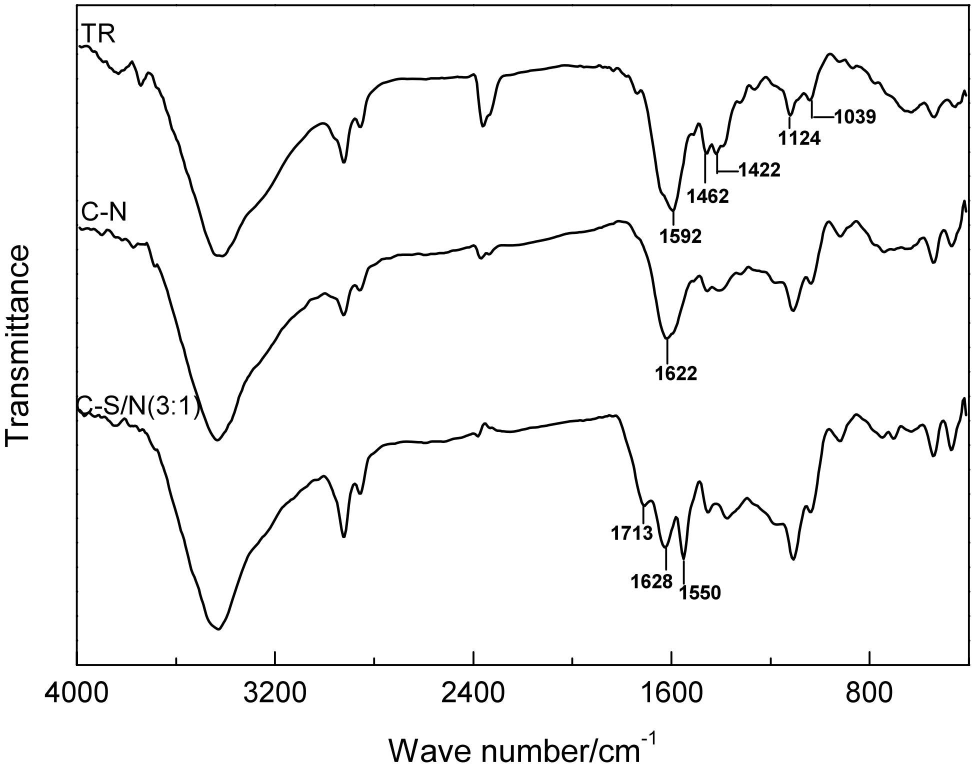


Fig. 1 FT-IR spectra of TR, C-N and C-S/N(3:1)

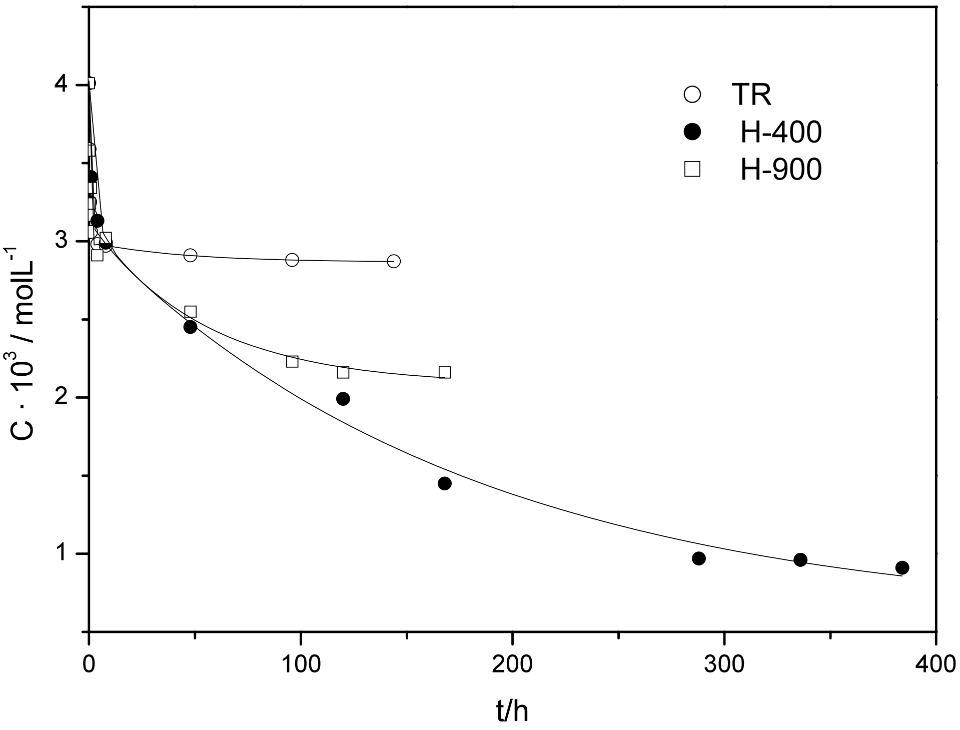
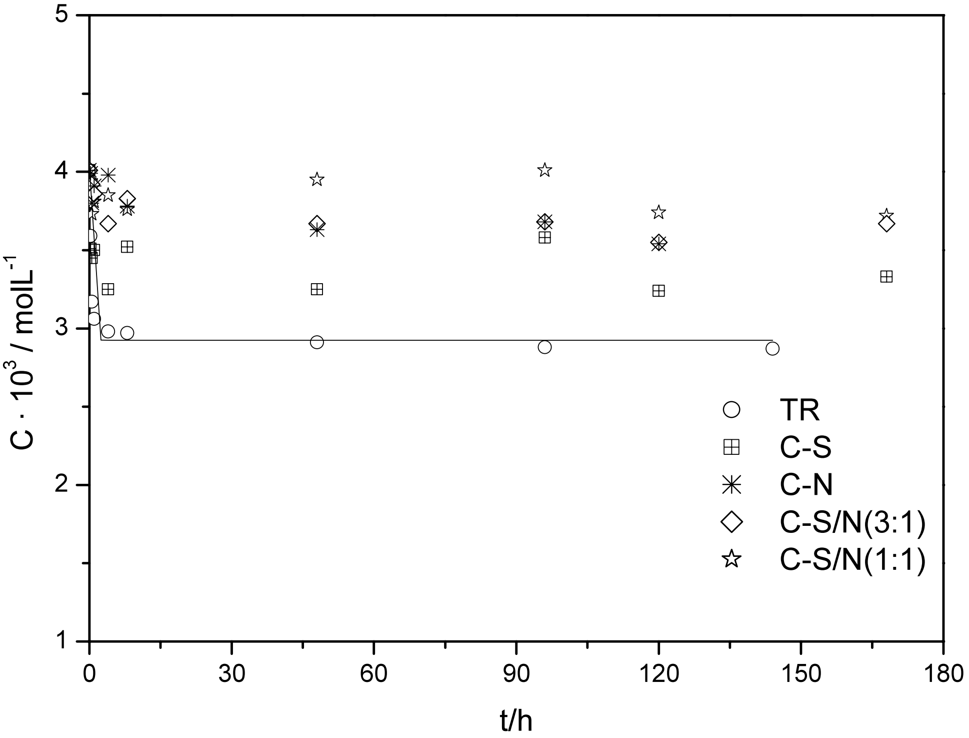


Fig. 2 Adsorption of lead from aqueous solution at pH 5.7. Variation of the solution concentration with contact time. Adsorbents: TR, H-400 and H-900

very high at pH 2.0. Moreover, the aquo-Pb^{2+} cation in all likelihood is a large size ion than the hydrated proton. These factors must give rise to an increased adsorption probability of H_3O^+ with respect to Pb^{2+}.

For the lead solutions at higher pHs a strong influence of not only solution pH but of also of the adsorbent on adsorption kinetics is observed. Figures 2 and 3 show the plots of C against t for the adsorption of lead in aqueous solution

Fig. 3 Adsorption of lead from aqueous solution at pH 5.7. Variation of the solution concentration with contact time. Adsorbents: TR and CAs prepared by chemical activation of TR



at pH 5.7 on TR, H-400 and H-900 and on a number of the chemically prepared CAs, respectively. The plots obtained for the remaining CAs have been omitted for the sake of brevity. It is seen that C first sharply decreases with t until 8 h for all adsorbents, including TR. Then, for longer adsorption times, C remains constant for TR and significantly decreases for H-400 and H-900. For the rest of the CAs the experimental points scatter, thereby being deviated in an important manner from the linearity. Furthermore, the plots stand noticeably above the plot for TR.

The above results indicate that the adsorption process of lead on TR and the CAs consists of two stages. The first one is very fast and must occur on easily accessible surface adsorption sites, likely located on the external surface and on large pore walls. The second one is important only for H-400 and H-900, being much slower than the first one. The deceleration of the adsorption process after a few hours of contact between the phases have elapsed, may be connected with the diffusion process of the adsorptive in narrow micropores of the adsorbent. It would be more hindered for H-400 than for H-900 as equilibration in the adsorption system took a longer time for the former CA. On the other hand, the constancy in C for TR accords with the poorly developed microporosity in this material.

The dispersion observed in the C–t experimental data for a series of CAs denotes a low stability of the adsorbed state because of a marked influence of the bulk of the Pb^{2+} solution. If so, the higher stability for TR than for the aforesaid CAs would be related to their surface chemistry and strength of the adsorbate/adsorbent interactions. From the decrease produced in the adsorption of lead for such CAs as compared to TR it is clear that the chemical treatments of TR with H_2SO_4, HNO_3 and H_2SO_4/HNO_3 to a significant extent caused a surface deactivation of the material for the adsorption of lead. It is attributable to the protonation of basic surface positions of TR under the action of the acidic reagents. This interpretation of the results is consistent with the competition between H_3O^+ and Pb^{2+} that presumably existed for the adsorption from the solution at pH 2 as in this instance the protonation of surface sites of the adsorbents by H_3O^+ would also prevent lead from its adsorption.

For the adsorptive solution at pH 12.6 the adsorption of lead is also a rapid process for the first 8 h for all adsorbents, as shown by the great slope of the C–t plots (Figs. 4–6). Also notice (see Figs. 2, 3 for comparison purposes) that the decrease produced in C is greater for the solution at pH 12.6 than for the solution at pH 5.7. Accordingly, the adsorption process of lead was speeded up at pH 12.6. Because at this pH Pb^{2+} must be mostly as $Pb(OH)_3^-$ (Baes and Mesmer 1976) in the adsorptive solution and because the electrostatic interaction of $Pb(OH)_3^-$ with the molecular dipole of water must be weaker than for Pb^{2+}, it appears that the diffusion of the $Pb(OH)_3^-$ ion in the bulk of the solution was facilitated and as a result the adsorption process was accelerated at such a high pH, as compared to lower pHs.

After the short liquid/solid contact time of 8 h, C remains nearly constant for TR and a larger number of the CAs. For H-400 and H-900, however, C varies with t. For H-400,

Fig. 4 Adsorption of lead from aqueous solution at pH 12.6. Variation of the solution concentration with contact time. Adsorbents: TR, H-400 and H-900

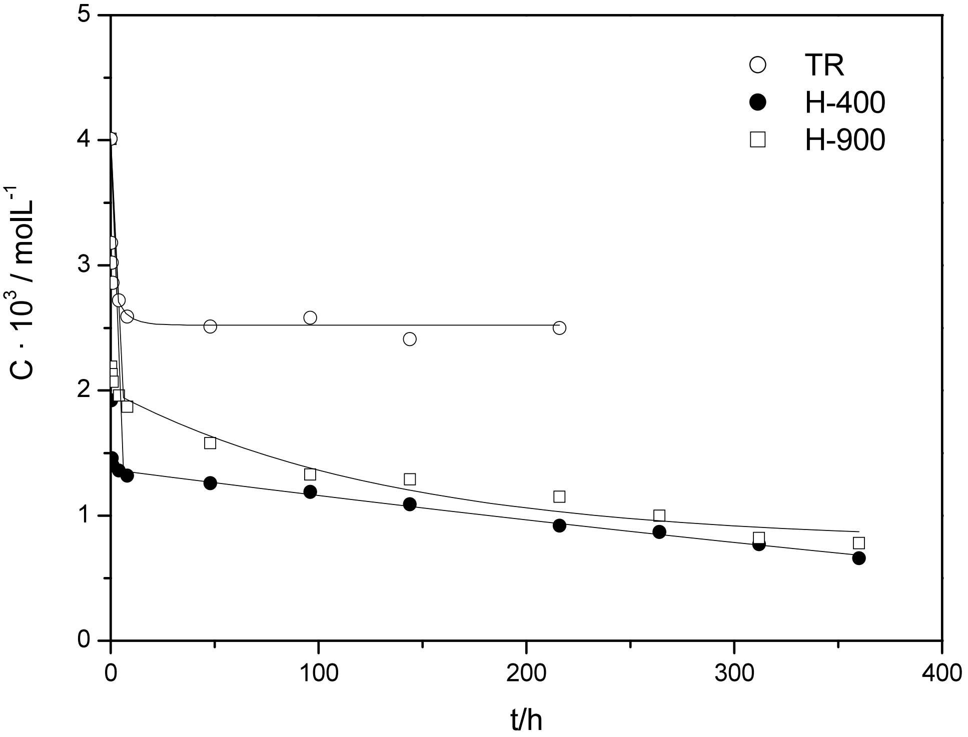
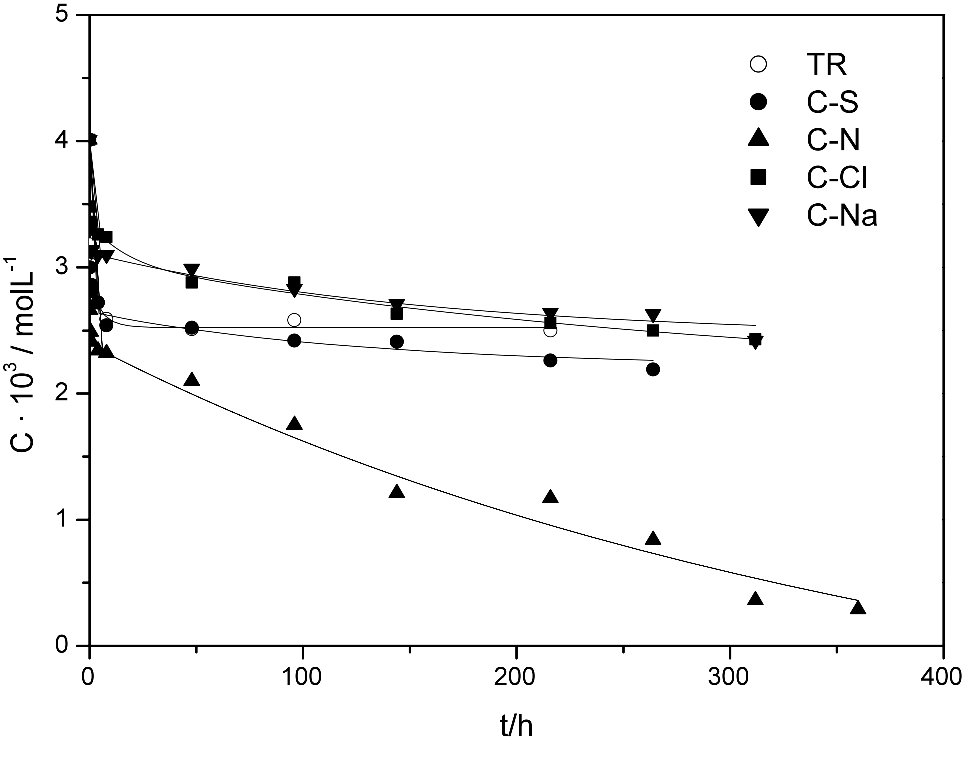


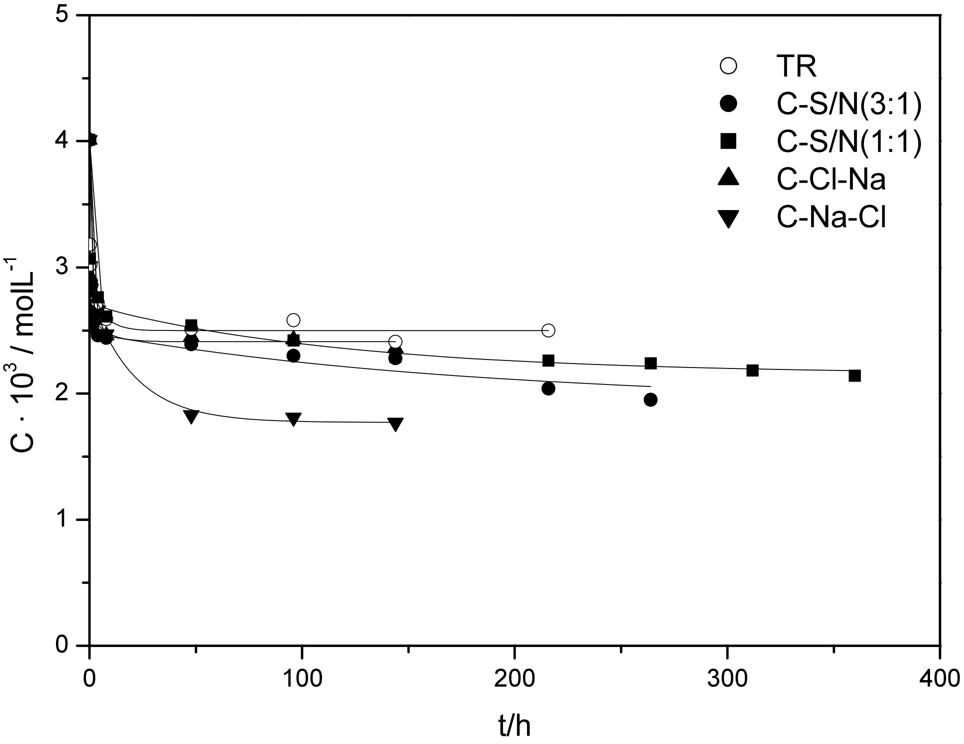
Fig. 5 Adsorption of lead from aqueous solution at pH 12.6. Variation of the solution concentration with contact time. Adsorbents: TR, C-Cl, C-N, C-S and C-Na



specially, the variation of C is much less marked at pH 12.6 than at pH 5.7. This suggests that at pH 12.6 a fraction of the surface active sites of the adsorbents were occupied by the adsorbate a shorter adsorption times or there was restriction to the adsorption of $Pb(OH)_3^-$ in narrow micropores of the adsorbent.

Figure 5 shows that the second adsorption stage is much slower for C-N than for the rest of the adsorbents. As de-

Fig. 6 Adsorption of lead from aqueous solution at pH 12.6. Variation of the solution concentration with contact time. Adsorbents: TR, C-S/N(1:1), C-S/N(3:1), C-Cl-Na and C-Na-Cl



scribed above, the treatment of TR with HNO_3, which is strong oxidant, resulted in the creation of a small fraction of micropores and in the formation of oxygen surface groups. These groups may concentrate in narrow pores and as a result render difficult the diffusion of $Pb(OH)_3^-$ and as a last resort slow down the adsorption process. The fact that the aforesaid kinetic behavior exhibited by C-N is not observed for C-N, C-S/N(3:1) and C-S/N(1:1) (Fig. 6) may be connected with steric hindrance effects associated with the presence of nitrogen surface groups in narrow micropores of these CAs. If so, the nitrogen surface groups would play a more decisive role in controlling the adsorption process of lead for prolonged adsorptive solution/adsorbent contact times than the oxygen surface groups.

For C-Na-Cl a high adsorption of lead occurs rapidly (see Fig. 6). In the case of this CA the ultimate treatment of the NaOH-treated product with HCl may cause protonation of basic surface sites, this leading to a reduction in the negative surface charge of the adsorbent which would make it possible the adsorption of a negative ion such as $Pb(OH)_3^-$. Protonation should be an irreversible process since, otherwise, the negative surface charge could be reestablished on the product treated with HCl by action of the OH^- ion present in the adsorptive solution brought into contact with the adsorbent.

To estimate the specific rate constant for the adsorption of lead from aqueous solution at both higher pHs, data of q_t against t were first fitted to the Lagergren equation (Lagergren and Svenka 1898). The values of r thus obtained were low and hence it was considered that the adsorption process is not first-order (Jain et al. 2003). Accordingly, k_2 was then calculated using expression (1) (Ho and McKay 1999),

$$(t/q_t) = (1/k_2 q_a^2) + (1/q_a)t \tag{1}$$

Since for TR and a number of CAs the adsorption process from the kinetic standpoint is only sensitive in the first stage, expression (1) was applied to the $q_t - t$ data obtained in the time interval between 0 and 8 h. For H-400, H-900 and C-N, as the adsorption of lead varies significantly for longer contact times, the $q_t - t$ data were fitted as well between 8 h and t_{mat}, which as a rule is a longer time than the equilibration time for each adsorption system. The calculated values of r and k_2 are listed in Tables 2 and 3 for the lead adsorption from the solution at pH 5.7 and 12.6, respectively. The high r values for all adsorption systems (i.e. usually above 0.99) indicate that the $q_t - t$ data fit very well to equation (11), as seen for example in Fig. 7. $k_{2,f}$ varies by the order H-400 > TR > H-900 (pH, 5.7) and C-Na > C-S/N(3 : 1) > C-Cl > C-N > H-400 > H-900, and so forth (pH, 12.6). For $k_{2,s}$ the sequences are H-900 > H-400 (pH, 5.7) and H-400 > H-900 ≫ C-N (pH, 12.6).

Tables 2 and 3 also list the calculated values of X_1 and X_2 for TR and the CAs. For TR X_1 is 0.26 mmol/g (pH 5.7) and 0.36 mmol/g (pH 12.6). These X_1 values indicate that the adsorption of lead for the short contact time of 8 h is already substantial even for the starting material used in the present study. Then TR can be regarded as a promising adsorbent to be used in the rapid removal of a significant amount of

Fig. 7 Ho and McKay plots for the adsorption of lead from aqueous solution at pH 12.6

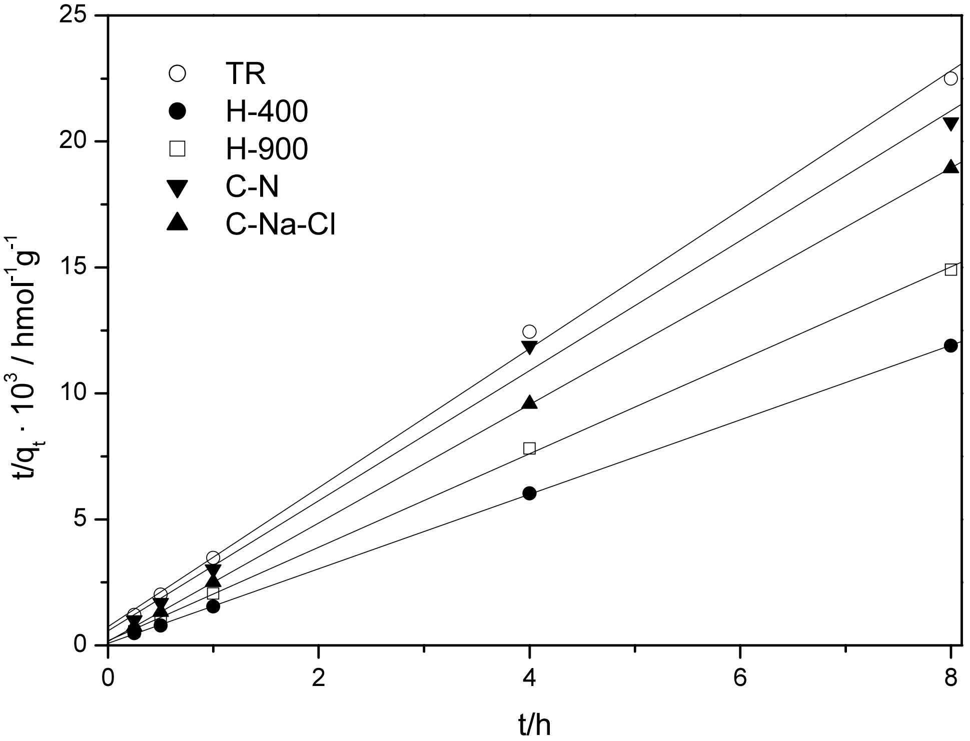


Table 2 Adsorption of lead in aqueous solution at pH 5.7. Specific adsorption rates and amounts

Sample	$k_{2,f} \times 10^{-3}$ (g mol^{-1}h^{-1})	r_f	$k_{2,s}$	r_s	t_{mat} h	X_1 mmol Pb^{2+}/g CA	X_2 mmol Pb^{2+}/g CA
TR	17.02	0.9994				0.26	0.28
H-400	92.32	0.9953	22.03	0.9900	360	0.26	0.77
H-900	13.48	0.9960	177.03	0.9983	168	0.25	0.46

Table 3 Adsorption of lead in aqueous solution *t* pH 12.6. Specific adsorption rates and amounts

Sample	$k_{2,f} \times 10^{-3}$ (g mol^{-1}h^{-1})	r_f	$k_{2,s}$	r_s	t_{mat} h	X_1 mmol Pb^{2+}/g CA	X_2 mmol Pb^{2+}/g CA
TR	9.66	0.9990			218	0.36	0.38
H-400	28.21	0.9999	90.16	0.9980	360	0.67	0.84
H-900	19.11	0.9975	63.95	0.9789	360	0.54	0.81
C-S	11.77	0.9979			360	0.37	0.45
C-N	35.84	0.9999	19.44	0.9789	264	0.42	0.93
C-S/N(3:1)	48.40	0.9999			264	0.39	0.51
C-S/N(1:1)	13.12	0.9985			360	0.35	0.47
C-Cl	37.16	0.9999			312	0.19	0.40
C-Na	79.50	0.9999			312	0.23	0.40
C-Cl-Na	17.55	0.9993			144	0.39	0.41
C-Na-Cl	11.60	0.9975			144	0.30	0.56

lead in aqueous solution. For H-400 and H-900, as compared to TR, the X_1 values show that the adsorption of lead occurs to a similar extent (pH, 5.7) or is greatly enhanced (pH, 12.6). Moreover, X_2 is very high for H-400 (pH, 5.7) and for H-400 and H-900 (pH, 12.6). For the solution at pH 12.6, specifically, X_1 and X_2 are higher for H-400 than for H-

900. From these results it is apparent that the CAs prepared by heating TR, in particular H-400, under a controlled pH of the initial lead solution are good adsorbents to be used whenever a fast, or extensive, or both lead removal from aqueous solution is required.

For the CAs prepared by chemical methods, as compared also to TR, X_1 is lower for C-Cl, C-Na and C-Na-Cl, similar for C-S and C-S/N(1:1), and slightly higher for C-Cl-Na, C-N and C-S/N(1:1). X_2 is however higher for the CAs, in particular for C-N. For this C-N it is as high as 0.93 mmol g^{-1}. Of the CAs prepared in the present study, therefore, C-N is the most effective to remove lead from the aqueous solution at pH 12.6 provided that the liquid/solid contact is maintained lengthily. The high X_2 for C-N is worth noting, as it denotes that the treatment of TR with HNO_3 results in the formation of oxygen surface groups which not only have an unfavorable influence on the kinetics of the adsorption process of lead, as seen above, but also, on the contrary, they behave as active sites towards lead as long as its adsorption occurs as $Pb(OH)_3^-$.

4 Conclusion

From the above results it may be concluded that, using discarded TR and CAs prepared from this waste by thermal and chemical methods, the rapid removal of a relatively great amount of lead from aqueous solution is possible. Adsorption kinetics and amounts depend on pH of the lead solution. When the adsorptive solution at pH 2 is used, the adsorption of lead is not measurable. The increase in pH of the lead solution from 5.7 to 12.6 gives rise to a speeding up of the adsorption process and to an increase in the extent to which it occurs. For the solution at pH 12.6, the amount of lead adsorbed for an adsorption time of 8 h is 0.36 mmol g^{-1} for TR, 0.67 mmol g^{-1} for H-400, 0.54 mmol g^{-1} for H-900, and 0.42 mmol g^{-1} for C-N. After such adsorption time, the adsorption process is slower for H-400 and H-900 and, in particular, for C-N. For this CA, the amount of lead adsorbed is 0.93 mmol g^{-1}(i.e. the adsorption percentage is 93 wt%) for a liquid/solid contact time of 264 h. The presence of narrow micropores in H-400 and H-900 and the formation of oxygen/nitrogen surface groups in such pores for C-N, C-S/N(3:1) and C-S/N(1:1) seem to be the factors that control the adsorption process of lead for adsorption times longer than 8 h.

Nomenclature

TR	tire rubber
CA/s	carbonaceous adsorbent/s
H-400	CA prepared by heat treatment of TR at 400 °C
H-900	CA prepared by heat treatment of TR at 900 °C
C-S	CA prepared by chemical treatment of TR with H_2SO_4
C-N	CA prepared by chemical treatment of TR with HNO_3
C-S/N(3:1)	CA prepared by chemical treatment of TR with 3:1 H_2SO_4/HNO_3
C-S/N(1:1)	CA prepared by chemical treatment of TR with 1:1 H_2SO_4/HNO_3
C-Cl	CA prepared by chemical treatment of TR with HCl
C-Na	CA prepared by chemical treatment of TR with NaOH
C-Cl-Na	CA prepared by chemical treatment of TR successively with HCl and NaOH
C-Na-Cl	CA prepared by chemical treatment of TR successively with NaOH and HCl
S_{BET}	BET surface area (N_2 adsorption isotherm)
W_0	micropore volume (N_2 adsorption isotherm, Dubinin-Radushkevich equation)
$V_{me\text{-}P}$	mesopore volume (mercury porosimetry)
V_{ma}	macropore volume (mercury porosimetry)
ν	stretching vibration mode
C	Pb^{2+} solution concentration (mol L^{-1})
t	adsorption time (h)
q_t	amount of lead adsorbed per adsorbent mass unit (mol g^{-1})
q_a	fitting constant (mol g^{-1})
k_2	second-order adsorption rate constant (g mol^{-1} h^{-1}): f, first adsorption stage; s, second adsorption stage
r	linear correlation coefficient: f, first adsorption stage; s, second adsorption stage
t_{mat}	maximum adsorption time (h)
X_1, X_2	amounts of lead adsorbed (mmol Pb^{2+}/g adsorbent) at $t = 8$ h and $t = t_{mat}$

Acknowledgement Financial support from the Spanish Ministerio de Educación y Ciencia on project CTM2005-08100/TECNO is gratefully acknowledged.

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