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A comparison on efficiency of virgin and sulfurized agro-based adsorbents for mercury removal from aqueous systems

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Abstract Mercury adsorption by sulfur impregnated adsorbents seems to be one of the most efficient ways for removal of this toxic metal ion from wastewater and atmosphere. The aim of this work was to develop a method for preparation of low-cost sulfurized adsorbent from agricultural wastes; this approach combines two stages of (i) chemical activation with phosphoric acid and (ii) impregnation with powdered sulfur, in one step only. The physico-chemical properties of sulfurized adsorbent (AC-S) were determined with BET, FT-IR, Eschka method and $\mathrm{pH_{PZC}}$ measurements, and compared with those of the virgin sample (AC). It was found that sulfurization according to this method can introduce about 8 wt.% sulfur into the structure of adsorbent, in the forms of C–S, S–H, S–S and S=O functional groups. Although during the sulfur introduction processes, a decrease in surface area and micropore volume of the sulfurized adsorbent is to be expected, not only such decrease did not occur in this work, but a large increase in microporosity was seen. Thereupon, both the sulfur functionalities and extended microporosity of AC-S lead to higher capability of this sample for mercury adsorption rather than AC. Finally, the kinetics and equilibrium of mercury adsorption from aqueous solutions were studied for AC and AC-S.

Keywords Activated carbon · Sulfur impregnation · Sulfurized adsorbent · Mercury · Kinetics · Isotherm

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Nomenclature

B	Constant of D-R isotherm related to energy, ($\mathrm{mol^2/J^2}$)
C_0	the solute concentration at time $t = 0$, (mg/l)
C_t	the solute concentration at time t, (mg/l)
C_e	the solute concentration at equilibrium, (mg/l) [in D-R model (g/g)]
e	Polanyi potential in D-R model
E	Free energy of adsorption, (J/mol)
h	$(= k_2 q_e^2)$ the initial sorption rate, (mg/g min)
k_1	Pseudo-first-order adsorption rate constant, (1/min)
k_2	Pseudo-second-order adsorption rate constant, (g/mg min)
K_F	Freundlich empirical constant, $(\mathrm{mg/g})(\mathrm{mg/l})^{-1/n}$
K_L	Langmuir empirical constant (l/mg)
K_T	Equilibrium binding constant corresponding the maximum binding energy, (l/mg)
n	the exponent in Freundlich isotherm
N	the number of runs
p	the number of model's parameters
$q_{i,\mathrm{exp}}$	the amount of solute adsorbed on the adsorbent observed from the ith run of experiment, (mg/g)
$q_{i,\mathrm{calc}}$	the amount of solute adsorbed on the adsorbent estimated from the model for corresponding $q_{i,\mathrm{exp}}$, (mg/g)
q_t	the amount of solute adsorbed at time t, (mg/g)
q_e	the amount of solute adsorbed at equilibrium, (mg/g) [in D-R model (mol/g)]
q_m	Monolayer adsorption capacity (in Langmuir model (mg/g)), (in D-R model the theoretical monolayer saturation capacity (mol/g))
R	Universal gas constant, (8.313 J/mol K)
R^2	Correlation coefficient
RMSE	Root mean squared error function
t	Time, (min)

T Absolute temperature, (K)
ΔQ the variation of adsorption energy, (kJ/mol)

1 Introduction

Mercury and its compounds, as the most hazardous water pollutants cause several health problems to human beings because of their severe toxicity and carcinogenicity even at low concentrations (UNEP 2008; U.S. EPA 1997). Various treatment techniques have been reported and applied for removal of such heavy metals from industrial wastewaters including precipitation (Kurniawan et al. 2006; U.S. EPA 1980; Ayres et al. 1984), ion-exchange (Chiarle et al. 2000; Yang and Renken 2000), membrane processes (Tang et al. 2007; Srisuwan and Thongchai 2002; Bessbousse et al. 2010), adsorption (Basha et al. 2009; Bayramoglu and ArIca 2008; Bhatnagar and Sillanpää 2010; Di Natale et al. 2006; Ekinci et al. 2002; Olivares-Marin et al. 2008; Shafaei et al. 2007) etc. Most of these methods suffer from drawbacks like high capital and operational cost and there are also problems in disposal of the residual metal sludge (Namasivayam and Sangeetha 2006). In numerous researches carried out in this field (Basha et al. 2009; Bayramoglu and ArIca 2008; Bhatnagar and Sillanpää 2010; Di Natale et al. 2006; Ekinci et al. 2002), it is established that adsorption using activated carbons and especially low cost adsorbents could be a satisfying technique for the removal of trace amounts of metal ions from dilute aqueous systems in the final steps of wastewater treatment processes. Because of the generic porous and chemical structure, virgin activated carbons are able to adsorb most of the pollutants in the wastewater, and so they are not very selective adsorbents towards mercury. But their capacity towards a special material like mercury could be significantly increased by impregnation of adsorbent with a material that chemically reacts with, and holds, the mercury (Mohan et al. 2000; Krishnan and Anirudhan 2002a, 2002b; Ranganathan and Balasubramanian 2002). Surface chemical modification of adsorbents with the aim of promoting their ion exchange properties for stronger and selective adsorption of special compounds has attained great interest recently (Krishnan and Anirudhan 2008; Nam et al. 2003; Rios et al. 2003; Lee et al. 2004; Mersorb® Mercury adsorbents 2010). Previous studies have shown that introducing sulfur functionalities onto the surface of adsorbents can improve their mercury uptake capacity (Feng et al. 2006; Hsi et al. 2002; Wajima et al. 2009). This idea is inspired by Pearson rule; according to this theory, oxygen molecules which naturally exist on the surface of typical activated carbons are hard bases and react hardly with metal ions such as Hg^{2+} (soft acid). In contrast, sulfur is a soft base and its reaction with such metal ions is easier and stronger (Krishnan and Anirudhan 2002a, 2002b; Wajima et al. 2009). Due to the high cost of commercial activated carbons especially sulfurized ones, use of these adsorbents in industrial scale is not economical, and so presenting a new way for production of low-cost sulfurized adsorbents would be very valuable. In the present work, in order to reduce the operating cost of production of sulfurized adsorbent, a simple simultaneous chemical activation and sulfurization technique was applied. Furthermore using agricultural wastes as the carbonaceous precursor (Arjmand et al. 2006; Bhatnagar and Sillanpää 2010; Fouladi Tajar et al. 2009; Kaghazchi et al. 2010; Soleimani and Kaghazchi 2007) and applying the powdered sulfur prepared from Claus units of sour gas refineries as sulfurizing agent have caused to reach sulfurized adsorbent with a total cost much less than the commercial ones; because these raw materials are all available in minimal cost or even free. The efficiencies of produced adsorbents were investigated and compared from the viewpoint of mercury removal from aqueous solutions.

2 Experimental

2.1 Raw materials

The precursors used in this work, including carbonaceous raw materials and impregnating agents are as follows:

- Residues of licorice provided by Shiraz agricultural and industrial company; with the chemical composition of 56.5 wt.% cellulose, 22.5 wt.% lignin and 6.8 wt.% ash.
- Pistachio-nut shells prepared from domestic agricultural wastes; with the chemical composition of 42.0 wt.% cellulose, 13.5 wt.% lignin and 1.3 wt.% ash.

In this work, the adsorbents were prepared by chemical activation of a mixture of the above-said agricultural wastes. However, the reasons of selection of such mixture instead of individual materials have been explained in details in one of the previous works of the authors (Kaghazchi et al. 2010); but in short it can be mentioned that using both hard and soft biomass wastes together and as a mixture, to produce activated carbons, can be useful to reach adsorbents with higher quality and also can solve the disposal problems of these wastes. Licorice residue is a type of high carbon content biomass wastes which are widely available in Iran with little or no value, and also present disposal problems. Previous studies (Madadi Yeganeh et al. 2006) have shown that activation of such soft materials leads to adsorbents with relatively high surface area, but they also show some weaknesses including high ash content, low bulk density and low mechanical strength. One of the ways to strengthen the structural properties of final adsorbent is using a kind of hard shells like pistachio-nut shells along with licorice residues as the parent material (Kaghazchi et al. 2010). In the previous work (Kaghazchi et al. 2010) three weight ratios were

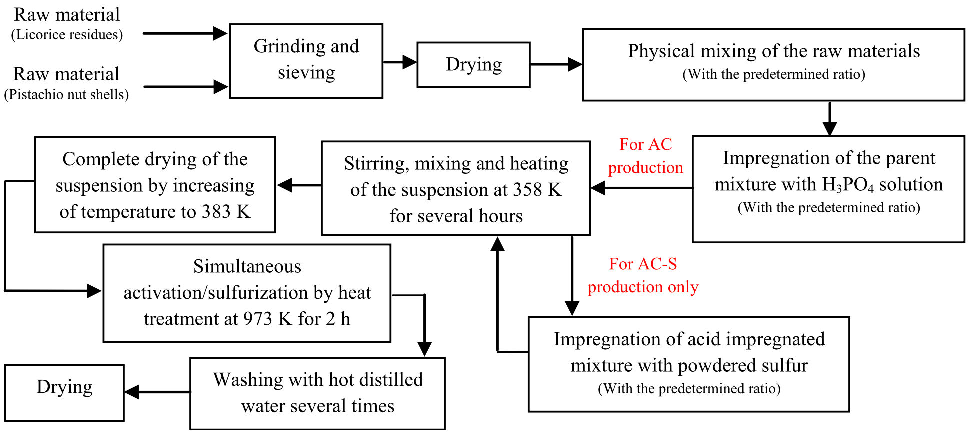

Fig. 1 Flow diagram of preparation procedure of AC and AC-S

tested for these two materials in the feedstock; 30:70, 50:50 and 70:30 for licorice residues to pistachio nut shells, and the optimum level for this factor was obtained according to an experimental design method (Taguchi). The experiments which have led to selection of the optimized ratio (30:70), characterization of the produced adsorbent and its advantages to adsorbents produced from individual materials have been explained in details in that work (Kaghazchi et al. 2010).

- Phosphoric acid of industrial grade; which was used as the chemical impregnating agent.
- Powdered elemental sulfur, the by-product of Claus unit of Tehran refinery which was used for sulfurization.

2.2 Preparation of virgin and sulfurized adsorbents

AC and AC-S adsorbents were prepared using the raw materials mentioned, according to the procedure discussed below step by step. For easier understanding, a flow chart of this procedure is also shown in Fig. 1.

- Grinding the primary carbonaceous materials (pistachio-nut shells and residues of licorice) using a laboratory mill and sieving by a conventional sieve-shaker to obtain the size fraction between 12 and 16 mesh number,
- Drying the materials at 383 K for 5 h; and mixing them with the predetermined weight ratio (the optimized value of 30:70 for licorice residues to pistachio shells, pointed in Sect. 2.1) to reach the primary mixture,
- Adding 15 g of this mixture to 150 ml of phosphoric acid solution with the impregnation ratio of 1:1 (impregnation ratio means the weight ratio of pure H_3PO_4 to carbonaceous raw material),
- Stirring and heating of the suspension at 358 K (8 h for AC and 4 h for AC-S),
- This step is only allocated to AC-S production; after the previous step (4 h heating and stirring with H_3PO_4 solution at 358 K), powdered sulfur was added to the suspension with the weight ratio of 2:1 for sulfur to primary carbonaceous material. The suspension was again mixed and heated at 358 K for 4 h.
- Increasing the temperature to complete the process of drying and achieving a well mixed mixture;
- Heat treatment of the dried mixture in a programmable electrical furnace (Nabertherm Labothem) with the heating rate of 2.5 K/min to reach 973 K and holding time of 2 h under the inert atmosphere of N_2;
- Washing of the activated samples with hot distilled water sequentially several times, until no further change could be detected in the pH of washing solution;
- Drying of the leached adsorbents at 383 K for 4 h;

After drying, the samples were weighed to determine the production yield from dividing the weight of prepared activated carbons by the weight of the dried carbonaceous raw materials. The production yield of AC was obtained about 35 %, but in the case of AC-S this value was increased into 55 %. AC-S in addition to carbonaceous material has some amount of sulfur in its structure; therefore the higher yield could be expected in this case.

As it was pointed before, the prominent point of this work was the use of a simple simultaneous chemical activation/sulfurization technique which represents energy and time saving procedure for production of sulfurized adsorbent. Also utilizing low cost agricultural wastes and sulfur by-product of Claus units both help to produce an economic sulfurized adsorbent.

2.3 Characterization of virgin and sulfurized adsorbents

The porous texture of AC and AC-S was characterized by physical adsorption of nitrogen using an automatic volumetric apparatus (Quantachrom NOVA 1000) to measure N_2 isotherms at 77 K. Before every adsorption measurement, the samples were oven-dried overnight at 373 K, and after that were out-gassed at 383 K for 24 h. It is necessary to note that selection of such low temperature for degassing of sulfurized adsorbents is to avoid volatilization of the sulfur before measurements (Macias-Garcia et al. 2003; Hsi et al. 2001, 2002; Vitolo and Seggiani 2002). Also in order to reach a true comparison between AC and AC-S, both samples were outgassed at the same conditions. Nitrogen adsorption-desorption data were analyzed using the following methods: the BET (Brunauer, Emmett & Teller) method to calculate the specific surface area (S_{BET}); HK (Horvath-Kawazoe) and BJH (Barrett, Joyner & Halenda) methods to predict pore size distribution of micro and mesopores, respectively (Lowell et al. 2004). The total pore volume in each sample was evaluated from the amount of nitrogen adsorbed at the highest relative pressure examined. The mesopore volume was obtained by the BJH method as well as by subtracting the HK micropore volume from the total pore volume (Lowell et al. 2004). Apparent or bulk density of adsorbents—the mass of a unit volume of the sample including both the pores and the voids between the particles—was determined according to the method suggested by Ahmedna et al. (1997). The amount of sulfur attached into the structure of adsorbents was measured using Eschka method. In this standard analysis method, the amount of sulfur can be determined by measuring the amounts of $BaSO_4$ which forms as a result of treating of sulfur present in adsorbents with the Eschka mixture (Na_2CO, MgO) at 1073 K and then successively with Br_2 and $BaCl_2$ solution (Rump and Krist 1992). Both virgin and sulfurized samples were subjected to FT-IR analysis to elucidate and compare the predominant forms of functional groups available on the surface of produced adsorbents. Samples for FT-IR analysis were prepared by grinding a very small amount of adsorbent with KBr salt followed by compression between two stainless steel cylinders to form a thin transparent solid film. This film was subjected to direct scanning in an FT-IR spectrophotometer (Perkin Elmer model Paragon 1000PC) to determine the predominant forms of oxygen, sulfur and other possible groups on the carbon surface. The pH of zero point charge ($\mathrm{pH_{PZC}}$) of produced adsorbents was measured according to the method suggested by Noh and Schwarz (1989). In this method weighed amounts of carbon are added sequentially to a given volume of aqueous 0.1 N NaCl until pH of the solution does not change with further addition of carbon. This fixed value was taken as the $\mathrm{pH_{PZC}}$.

2.4 Mercury adsorption experiments

AC and AC-S adsorbents were tested for evaluating and comparing their mercury adsorption capacity from aqueous solutions in batch systems. Mercury stock solution (1000 ppm) was prepared by dissolving 1.354 g of mercuric chloride (Merck) in 10 ml nitric acid (Merck, 65 wt.%) and diluting it with deionized water to the volume of 1 l; this solution was further diluted to reach the favorite concentrations. It is proved that due to the abundant existence of chloride ions in natural environments, use of mercuric chloride for production of a synthetic sample of mercury contaminated wastewater gives a realistic and conservative estimation from real environment.

Kinetic studies were performed to describe rate of mercury uptake from aqueous solutions and determine the equilibrium time. For this series of experiments, 50 ml of 100 mg/l mercury solutions were treated with 0.1 g of adsorbents for 5, 10, 15, 20, 30, 45, 60, 90, 240, 360 and 540 min. Agitation of samples was carried out on an orbital shaker at 300 rpm and room temperature. At pre-decided time intervals, the supernatant was withdrawn, filtered, and analyzed for Hg (II) concentration using an atomic absorption spectrophotometer. The contact time and sampling intervals were selected based on preliminary experiments. The pH of solutions during the tests was maintained at the constant value of 8.0. For this reason, pH of suspensions was measured several times during the total duration of each experiment; with the lapse of time a decrease in the pH of solution was observed and so the adjustment to $\mathrm{pH} = 8$, was carried out by adding required amount of dilute NaOH solution (0.1 M). Selection of this value for pH was based on the results of a series of preliminary experiments (not shown here). According to these tests it was found that the mercury adsorption capacity of both adsorbents (AC and AC-S) increase from acidic to alkaline conditions. The maximum adsorption occurred about pH 8.0 and after that it became nearly constant, so this value was taken as the optimal value for further adsorption studies. Review of the literature on Hg (II) speciation diagram shows that in the presence of Cl^-, the dominant mercury species at this pH condition are the electro neutral molecules of $Hg(OH)_2$ and HgCl(OH) (Krishnan and Anirudhan 2002a; Anirudhan et al. 2009).

Equilibrium series of adsorption experiments were carried out to draw the adsorption isotherms, by shaking single solutions having various mercury concentrations (20, 50, 100, 150, 200 and 250 mg/l) and adsorbent dose of 2 g/l for 24 h. Other operating conditions such as temperature, agitation speed and pH of solutions were adjusted as the same as kinetic experiments. All the above-said experiments were repeated three times and the average values were reported.

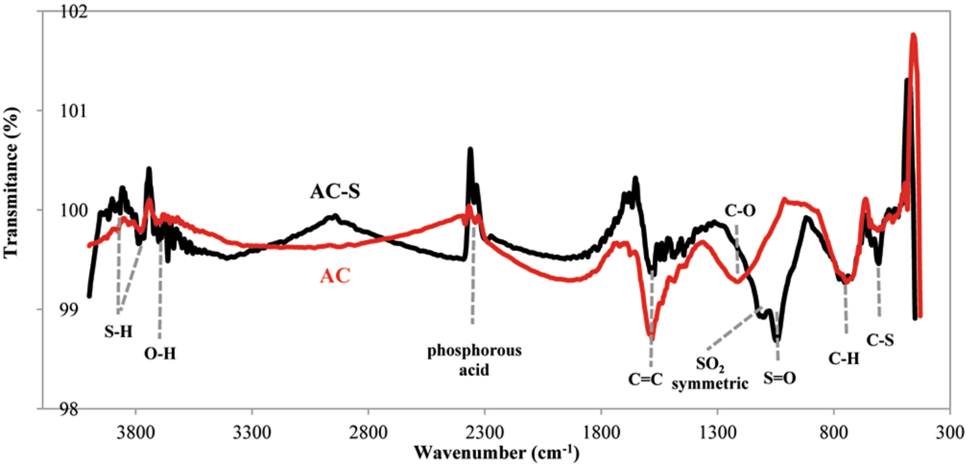

Fig. 2 FT-IR data of AC and AC-S

3 Results and discussion

3.1 Chemical properties of AC and AC-S adsorbents

The efficiency of sulfurization method used in this work, was evaluated by comparing the sulfur content of AC and AC-S. The amount of sulfur in AC-S was found about 8 wt.%, indicating the success of this method in entering sulfur into the structure of adsorbent. The inserted sulfur has formed different types of functionalities on the surface of AC-S, that some of them were determined by FT-IR analysis. Figure 2 depicts FT-IR scans of AC and AC-S, comparatively. For both adsorbents several peaks can be seen in the spectra coming from oxygenated groups; some of them are noted in Fig. 2. For example several peaks are available around 3600 cm^{-1} and about 1700 cm^{-1}, which belong to O–H and C=O bonds, respectively. They also showed peaks around 1600 cm^{-1}, which are related to the carbon skeleton and resulted from aromatic rings or carbon-carbon double bands (C=C). The peaks related to C–H groups are also located in the range of 700–800 cm^{-1}.The spectra of AC sample also shows a wide peak around 1200 cm^{-1} which may be related to C–O groups. Both adsorbents have peaks between 2300–2400 cm^{-1} which belong to the phosphorous acid and ester P–H stretching bonds. However during the washing stage it was tried to remove phosphorous molecules of H_3PO_4 from the structure of adsorbent completely, but it may be remained to some extent on the surface of adsorbents. In addition to the foresaid groups, several new bands can be seen in the spectra of AC-S; for example the small peak at about 500 cm^{-1} is related to S–S group and the peak around 610 cm^{-1} is the characteristic band of C–S group. There is also a large peak at 1046 cm^{-1} which is representative of presence of S=O group. Some peaks can be observed in the spectra of AC-S, in the range of 1400–1000 cm^{-1}, which may be related to the SO_2 (symmetric and asymmetric) stretching bands (Stuart 2004). It can be seen that the number and severity of peaks in the range of 4000–3700 cm^{-1} in the spectra of AC-S is more than AC; this may be related to the formation of S–H group on the surface of AC-S (Pouchert 1989). Although it is well established that surface modification of activated carbon with sulfurizing agents is promising for improving Hg (II) adsorption, more systematic work is needed to fully understand what type of functional groups on the surface of activated carbon is beneficial for Hg (II) adsorption and how it works. The review of literature among the few works have been done in this field, have shown that thiols (–S–H) are the most dominant binding groups for adsorption of mercury species from aqueous solutions (Wiederhold et al. 2010). Xia et al. (1998) revealed the importance of reduced sulfur functional groups (thiol (R–SH) and disulfide (R–S–S–R)/disulfane (R–S–S–H)) in the complexation of Hg (II). It was also established by Michelsen et al. (1975) that the sorption of mercury from aqueous solutions comes from the reaction of mercury with disulfide bonds in vulcanized rubber. Few researchers have claimed that the sulfonic acid functional groups can also be useful for mercury adsorption (Anirudhan et al. 2008). According to the literature, the authors believe that the most important groups in mercury (II) adsorption are S–H, S–S and to somewhat C–S and S=O. The values of pH$_{PZC}$ for AC and AC-S samples were measured as 5.4 and 4.3, respectively. The lower value of pH$_{zpc}$ of sulfurized sample indicated that the surface of AC-S has more acidic functional groups than AC, i.e. in addition to oxygenated acidic groups which are available on the surface of both samples, some amounts of sulfur groups that are naturally acidic, have been formed on the surface of AC-S. So it is less basic than AC, which can be considered as an advantage in the process of metal cations removal.

Table 1 The physical properties and porous structure and of AC and AC-S samples

Adsorbent	Bulk density (cm^3/g)	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Micropore volume, HK method (cm^3/g)	Mesopore volume (cm^3/g)		Average pore width (Å)	
					BJH method	V_{TOT}-V_{MIC}	Micro (HK)	Meso (BJH)
AC	0.32	1086	0.69	0.45	0.29	0.24	11	31
AC-S	0.55	1870	1.18	0.93	0.23	0.25	9	36

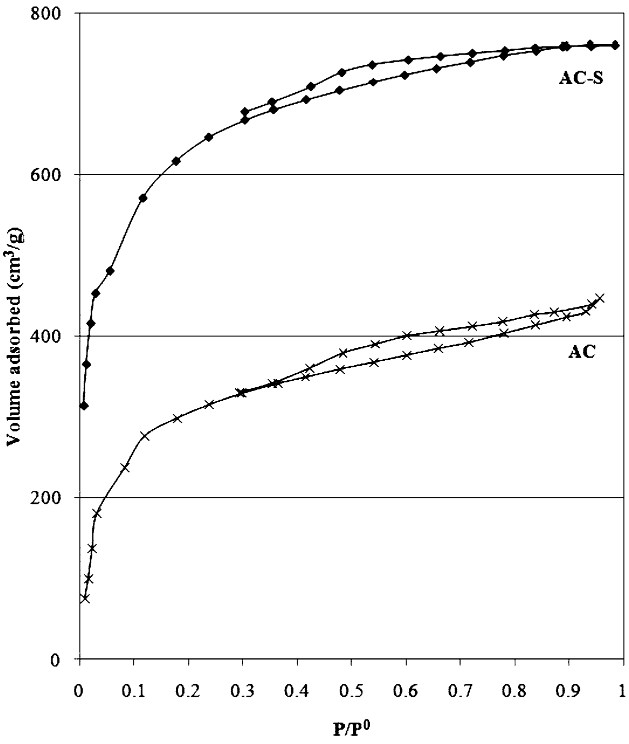

Fig. 3 N_2 adsorption-desorption isotherm at 77 K on AC (—×—) and AC-S (—♦—)

3.2 Physical properties of AC and AC-S adsorbents

The bulk densities of both samples are shown in Table 1; the higher bulk density of AC-S in comparison with AC is representative of the positive role of sulfur introduced into the structure of carbon in increasing its bulk density. The nitrogen adsorption-desorption isotherms of the two samples were obtained to acquire more information about the porosity. The isotherms have been depicted in Fig. 3. The adsorption isotherms of AC and AC-S, to a great extent, are similar to the type I isotherms (IUPAC classification) which characterize microporous adsorbents having relatively small external surface. The presence of hysteresis in both samples indicates the contribution of mesopores to the porosity. Hysteresis appearing in the multilayer range of physisorption isotherms is usually associated with pore filling (or capillary condensation) and pore emptying (or capillary evaporation) in mesopore structures (Sing et al. 1985). Considering the shape of hysteresis loops (Fig. 3), in which the two branches remain nearly horizontal and parallel over a wide range of P/P_0, it may be concluded that the appeared loops in both adsorbents are of type H_4 (IUPAC classification) which is often associated with narrow slit-like pores. So it can be concluded that the produced adsorbents have heterogeneous pore size distributions (having a combination of micro and mesopores). As it can be seen from the data of Table 1, AC-S has a higher BET surface area and total pore volume than AC; this may be due to the higher proportion of microporosity in the total pore network of this sample. The micropore volume of the samples were calculated by HK method (Lowell et al. 2004); from the data, it can be estimated that about 65 % of porous structure volume of AC belongs to micropores, but in the case of AC-S this value increases to 80 %. For both samples, the mesoporous volume obtained by BJH method was very close to the values calculated from the subtracting the HK micropore volume from the total pore volume; this indicates the good accuracy of the methods applied for interpreting of the isotherms. In most of the works carried out in this field, exposure of adsorbent to sulfurizing agent has led to a decrease in the surface area of adsorbent (Fouladi Tajar et al. 2009; Hsi et al. 2001, 2002; Korpiel and Vidic 1997; Krishnan and Anirudhan 2002a, 2002b; Liu et al. 2000; Skodras et al. 2002, 2007), might be due to creation of sulfur deposits at the pore openings and blocking the access to the narrower inner pores. In contrast, in the present work, the use of sulfur along with H_3PO_4 helps to develop the microporosity of the final adsorbent. In this method, sulfur can well diffuse into the interior channels of the botanic structure, which have been hydrated and swelled by H_3PO_4 impregnation before; in fact acid helps to open the paths for sulfur, to reach the inner structure of carbonaceous material more easily. The effect of introduced sulfur on the porous structure of sulfurized adsorbent may be different, depending on where it is trapped. Some amounts of sulfur which has been remained in the very interior parts of the impregnated material, has not any access to the outer surface and the available heteroatoms (like oxygen and hydrogen) and so during the activation stage cannot be converted into suitable functional groups. Since activation with H_3PO_4, often produces large amount of mesoporosity in the final adsorbent (Williams and Reed 2004;

Table 2 Comparison of kinetic parameters for adsorption of mercury species onto AC and AC-S

Model	Equation	Linearized form	Parameters	
			AC	AC-S
Pseudo-first order kinetic model	$q_t = q_e(1 - \exp(-k_1 t))$	$\ln(q_e - q_t) = \ln(q_e) - k_1 t$	$k_1 = 0.009$ $q_{e,\text{calc.}} = 12.97$ $q_{e,\text{exp.}} = 47.00$ $R^2 = 0.9145$ $\text{RMSE} = 36.40$	$k_1 = 0.016$ $q_{e,\text{calc.}} = 5.06$ $q_{e,\text{exp.}} = 49.94$ $R^2 = 0.8406$ $\text{RMSE} = 48.90$
Pseudo-second order kinetic model	$q_t = q_e \frac{q_e k_2 t}{1+q_e k_2 t}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$k_2 = 0.003$ $q_{e,\text{calc.}} = 47.39$ $q_{e,\text{exp.}} = 47.00$ $h = 6.71$ $R^2 = 0.9999$ $\text{RMSE} = 1.51$	$k_2 = 0.014$ $q_{e,\text{calc.}} = 50.00$ $q_{e,\text{exp.}} = 49.94$ $h = 34.72$ $R^2 = 1$ $\text{RMSE} = 1.05$

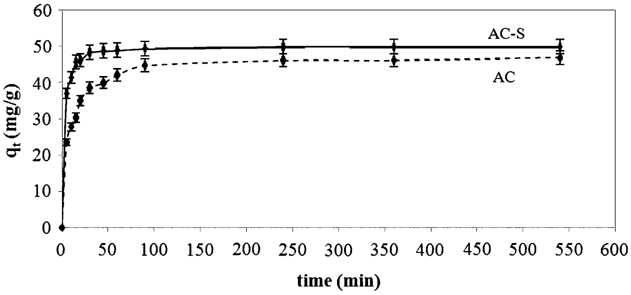

Fig. 4 Time dependence of mercury adsorption capacity of AC (- -●- -) and AC-S (—♦—)

Molina-Sabio and Rodríguez-Reinoso 2004), it is probable that in the process of AC-S production, the trapped sulfur, filling some space and narrowing the produced mesoporosity, facilitates the converting of large micro- and mesopores into narrow micropores. With this claim, it is possible to justify why the value obtained for average micropore width (calculated by HK method) for AC-S is lower than AC. On the other hand, a portion of sulfur which is located in the mesopores and closer to the outer surface of the material may react easily with heteroatoms and produces functionalities, which have not such influences on the porosity of adsorbent. During the heating, the reaction of some amounts of this sulfur with oxygen molecules—available on the surface of impregnated biomass—and producing SO_2 is also probable. The exit of SO_2 from the mesopores may lead to widening them. Such mechanism may be the reason of the larger average mesoporous width (obtained by BJH method) of AC-S than AC.

3.3 Kinetics of mercury adsorption for AC and AC-S adsorbents

According to the data of Fig. 4 which shows and compares the time dependence of mercury adsorption capacities of AC and AC-S, it can be concluded that AC-S reaches to equilibrium faster than AC. The necessary time to reach equilibrium for AC is about 100 min, whereas in the case of AC-S this value is only about 30 min.

The kinetic data were further analyzed to obtain the rate at which mercury species can be removed from solution by the adsorbents. This analysis was carried out using the pseudo-first order and the pseudo-second order rate models (Ho and McKay 1999; Lagergren 1898; Zhao et al. 2009). The validity of each model was checked by fitness of straight lines (R^2 values); moreover the root mean squared error function (RMSE) was employed to support the best-fit adsorption model (Table 2). RMSE can be represented as follows:

$$\text{RMSE} = \sqrt{\frac{1}{N-p}\sum_{i=1}^{N}(q_{i,\text{exp}} - q_{i,\text{calc}})^2} \tag{1}$$

The smaller RMSE value indicates the better fitting.

From Table 2, it can be seen that the experimental kinetic data do not show a good fit with the pseudo-first order model, and there is a large difference between the experimental and calculated q_e for both adsorbents. In contrast, in the case of pseudo-second order kinetic model, the extremely high correlation coefficient, relatively low value of RMSE and agreement of the calculated q_e with the experimental value suggest that the adsorption data for both adsorbents are well represented by this model. A comparison shows that the pseudo-second order rate constant (k_2) and initial sorption rate (h) for AC-S are higher than AC. The confirmation of pseudo-second order model means that adsorption behavior of both adsorbents has more agreement with the chemical adsorption. However it is not logical to postulate that the physical adsorption of mercury into the pores of such porous adsorbents is negligible. Because it is usually claimed that the physical adsorption inherently occurs with the higher rate than chemisorption (Bylina et al. 2009), the authors believe that the proportion of physical adsorption at the first minutes of process is higher than chemisorption. AC-S sample having more developed porosity and higher surface area, at the initial stages of contact, would be able to adsorb mercury with a higher rate; this may be the reason of the higher initial sorption rate (h) of AC-S. At the subsequent stages of adsorption, the contribution of chemisorption in the overall mechanism would become greater. It is known that sulfur functional groups and somewhat oxygenated groups are responsible sites for mercury chemisorption; the reason of higher overall mercury adsorption rate on AC-S may be related to the presence of both of these functionalities on its surface in comparison with AC which only has oxygenated groups. The data about the presence of different functionalities on these adsorbents are available in Sect. 3.1.

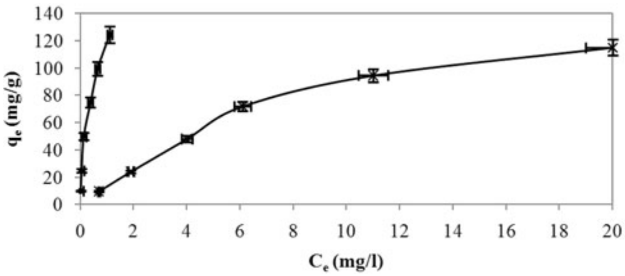

Fig. 5 Mercury adsorption isotherms for AC (—×—) and AC-S (—♦—)

3.4 Equilibrium of mercury adsorption for AC and AC-S adsorbents

The mercury adsorption isotherms for AC and AC-S are presented in Fig. 5. According to the shape of these curves and the Gile's classification (Giles et al. 1960; Hinz 2001), it may be concluded that the adsorption isotherm of AC is of 'L' type; however, the adsorption isotherm for AC-S is more close to the 'H' type. Showing AC isotherm as 'L' class indicates that mercury is strongly adsorbed on this sorbent, and that there is no competition from the solvent for sorption sites. In this model, as more sites of the adsorbent are filled, it becomes increasingly difficult for a solute molecule to find a vacant site; this point can also be observed from the shape of isotherms, so that initially the adsorption is quite rapid, and then followed by a slow approach to equilibrium at high concentrations. But in comparison, the shape of AC-S isotherm is almost close to the 'H' type. This type is a special case of 'L' curve, which its initial part is almost vertical. This type of isotherms implies to adsorption systems in which there is such high affinity between the adsorbent and adsorbate that just negligible amount of adsorbate remain in the solution.

The experimental data on equilibrium tests were further analyzed to fit various isotherm models including Langmuir, Dubinin-Redushkevich, Freundlich and Temkin. The linearized forms of the adsorption isotherms, the values of parameters involved, the correlation coefficients and the values of RMSE are given in Table 3.

Table 3 The comparison of the equilibrium parameters of adsorption of mercury species onto AC and AC-S

Model	Linearized equation	Parameters	
		AC	AC-S
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m . K_L} + \frac{C_e}{q_m}$	$K_L = 4.73$ $q_m = 140.8$ $R^2 = 0.9692$ $\mathrm{RMSE} = 92.46$	$K_L = 0.08$ $q_m = 188.7$ $R^2 = 0.9682$ $\mathrm{RMSE} = 83.50$
Dubinin-Redushkevich	$\ln q_e = \ln q_m - Be^2$ $e = RT \ln(1 + \frac{1}{C_e})$ $E = 1/\sqrt{2B}$	$B = 6 \times 10^{-9}$ $q_m = 0.014$ $E = 9129$ $R^2 = 0.9826$ $\mathrm{RMSE} = 12.79$	$B = 3 \times 10^{-9}$ $q_m = 0.009$ $E = 12910$ $R^2 = 0.9944$ $\mathrm{RMSE} = 6.31$
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$K_F = 127.67$ $1/n = 0.76$ $R^2 = 0.9695$ $\mathrm{RMSE} = 722.56$	$K_F = 14.65$ $1/n = 0.53$ $R^2 = 0.9873$ $\mathrm{RMSE} = 81.57$
Temkin	$q_e = \frac{RT}{\Delta Q}(\ln K_T + \ln C_e)$	$K_T = 1.42$ $\Delta Q = 73.60$ $R^2 = 0.9646$ $\mathrm{RMSE} = 8.59$	$K_T = 95.63$ $\Delta Q = 102.27$ $R^2 = 0.9443$ $\mathrm{RMSE} = 11.61$

3.4.1 Langmuir model

The Langmuir isotherm is based on monolayer adsorption on the active sites of adsorbent and constant heat of adsorption for all sites (Langmuir 1918; Hamdaoui and Naffrechoux 2007; Kosasih et al. 2010; Wang and Qin 2005). The validity of this model for equilibrium data of mercury adsorption onto AC and AC-S was investigated, and considering the values obtained for RMSE, it was found that the Langmuir model cannot provide an accurate description of experimental data. This suggests that mercury adsorption onto AC and AC-S is not limited to a monolayer sorption mechanism. The use of different raw materials and chemical impregnating agents in the preparation process of AC and AC-S causes non-homogeneous structures in the adsorbents. It means that in the structure of these adsorbents, there are lots of cavities with different sizes, which can trap mercury; there are also large amounts of functionalities of different types which some of them can chemically adsorb mercury. In addition, both of these carbons have some amounts of ash in their structure, which promote the non-homogeneity. It is highly probable that the different adsorption sites on the surface of these adsorbents are energetically nonequivalent, i.e. for being adsorbed on each site various amounts of energy is needed. So it may be concluded that for such adsorbents which do not have homogenous and even structures, the Langmuir model would not be very successful to interpret the sorption data (Langmuir 1918; House and Everett 1983; Krishnan and Anirudhan 2002b). So the conformity of other isotherm models with the equilibrium experimental data was studied.

3.4.2 Dubinin-Redushkevich model

In the previous section, it was concluded that the surface of produced adsorbents could not be considered homogeneous. In such cases, the assumption of dividing the total surface of adsorbents into several homogeneous subregions and fitting the Langmuir isotherm for each of local regions maybe not far from reality; under this condition, the Dubinin-Redushkevich equation would be a suitable model to fit the liquid-phase adsorption data (Seyhan et al. 2007; Wu et al. 2007). Therefore, fitness of experimental equilibrium data with D-R model was investigated, and the values of related parameters were determined (Table 3). Regarding to the values of R^2 and RMSE, it can be concluded that this model describe the data of mercury adsorption by both adsorbents accurately. One of the parameters of the D-R model—free energy of adsorption (E)—can be used for estimating the type of adsorption. It is established that when the magnitude of E is between 8 and 16 kJ mol^{-1}, the adsorption type can be explained by ion-exchange; and when the adsorption energy is lower than 8 kJ mol^{-1}, the type of adsorption can be considered as physical adsorption (Wu et al. 2007). From the data of Table 3, the values of E for both adsorbents are larger than 8 kJ mol^{-1}, so it can be inferred that the type of adsorption is described as ion-exchange. Moreover, the higher value of E for AC-S compared with AC shows that the sulfurized adsorbent adsorbs mercury species with more affinity, which is due to the stronger chemical reaction occurred between mercury ions and sulfur functionalities.

3.4.3 Freundlich model

The Freundlich equation is also among the isotherms applied to describe heterogeneous systems, and the main difference of this model with Langmuir isotherm is related to the heat of adsorption. As it was pointed before, according to the Langmuir model, heat of adsorption is constant in relation to the amount of coverage of adsorbent surface; in contrast in the Freundlich model, heat of adsorption in the layer decreases in a logarithmic trend with increasing the coverage degree (Freundlich 1906; Kosasih et al. 2010; Wang and Qin 2005; Oubagaranadin et al. 2007). So the applicability of Freundlich isotherm was analyzed by plotting $\log q_e$ versus $\log C_e$, and the related parameters of this model were obtained (Table 3). The relatively high values obtained for RMSE showed that the adsorption of mercury species onto none of the produced adsorbents obeys this model, and the assumption of logarithmic reduction of heat of adsorption is not correct for the studied cases.

3.4.4 Temkin model

Another model which was used to explain the experimental data of mercury adsorption is Temkin isotherm. This model is generally used to explore the energy distribution pattern. The derivation of the Temkin isotherm is based on that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation (Samarghandi et al. 2009; Wang and Qin 2005). It can be seen that the experimental data give good correlation coefficients and relatively low values for RMSE for this model, showing that Temkin isotherm can be considered as an appropriate description of mercury adsorption data over the concentration ranges studied. One of the constants of Temkin model, ΔQ, is related to the heat of adsorption; from the results of Table 3, it can be seen that the value obtained for this term in the case of AC-S is larger than AC, maybe due to the stronger adsorption of mercury species onto this sorbent.

4 Conclusions

The sulfurization method presented in this work was a simple and efficient procedure for producing low cost sulfurized adsorbents. The sulfurized adsorbent (AC-S) which was produced by heat treatment of agricultural wastes impregnated with H_3PO_4 and sulfur, in addition to having higher sulfur content (8 wt.%) showed a higher surface area and micropore volume, in comparison with the sulfur-free adsorbent (AC)—the virgin sample was produced by H_3PO_4 activation without the presence of sulfur. The higher surface area and especially the formation of sulfur functional groups like S–H, S–S and to somewhat C–S and S=O in AC-S, lead to a great increase in the mercury adsorption rate and capacity of this adsorbent from aqueous systems rather than virgin one. The present study also showed that mercury adsorption onto AC and AC-S follows the Dubinin-Redushkevich and Temkin isotherm models very well, but the accuracy of the data fitting with the Langmuir and Freundlich equations is less. It means that the mechanism of mercury adsorption onto these adsorbents is not limited to monolayer adsorption; and there are different adsorption sites with varying energies on the surface of these adsorbents, which their energy decreases linearly with degree of surface coverage. Kinetic data for both adsorbents fitted well in pseudo-second order model, confirming the adsorption of mercury ions by chemisorption and ion-exchange, which can also be evinced by energy of adsorption value, determined by D-R isotherm model.

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