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Adsorption of cadmium by sulphur dioxide treated activated carbon

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Abstract

Merck carbon (1.5 mm) was treated in three ways: heating from ambient temperature to 900 °C in SO_2; treatment at ambient temperature in SO_2; or successive treatments in SO_2 and H_2S at ambient temperature. All samples were then characterised and tested as adsorbents of Cd^{2+} from aqueous solution. The characterisation was in terms of composition by effecting ultimate and proximate analyses and also of textural properties by N_2 adsorption at −196 °C. Kinetics and extent of the adsorption process of Cd^{2+} were studied at 25 and 45 °C at pH of the Cd^{2+} solution (i.e., 6.2) and at 25 °C also at pH 2.0. The various treatments of the starting carbon had no significant effect on the kinetics of the adsorption of Cd^{2+}, but increased its adsorption capacity. The most effective treatment was heating to 900 °C, the adsorption in this case being 70.3% more than that of the starting carbon. The adsorption increased at 45 °C but decreased at pH 2.0 when compared to adsorption at 25 °C and pH 6.2, respectively.
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1. Introduction

The wastes of all kinds (industrial, domestic, agricultural, etc.) that are continually being dumped into the environment can represent a grave danger for public health due to certain of their components. Any cadmium present in these wastes, for example, will not disappear as a result of biological degradation, but will accumulate in the environment from becom-

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ing associated to organic or inorganic matter through processes of adsorption, formation of complexes, and chemical combinations [1–3]. Since cadmium is highly toxic to a great variety of living organisms including man [4], its poisonous effects being cumulative, investigations are currently being carried out aimed at the efficient elimination of cadmium from contaminated media [5,6].

One way to minimise the presence of heavy metals is to use activated carbon, which is a porous material that possesses a high adsorption ability towards adsorptive solutes in solution. Furthermore, the adsorption capacity of the carbon may be enhanced by treating it with sulphur compounds as this gives rise to the formation of surface carbon–sulphur complexes that facilitate the retention of metals [7–10], such as cadmium, that form a strong bond with sulphur [11].

In connection with the activity of the carbon–sulphur complexes in adsorption processes the most important factor is likely their chemical nature as this will determine the acid–base character of the carbon surface and hence the behaviour of the carbon in such processes. So far there have been many attempts to determine with precision the composition of the surface complexes based on carbon–sulphur bonding. Puri et al. [12,13] found that, independently of the chemical agent used in its surface fixation, the sulphur seemed in part to be retained on unsaturated centres and in part united to the carbon by interaction with functional groups that present carbon–oxygen bonds, whether with aliphatic carbon or with phenols and quinones.

The chemical composition of the carbon–sulphur surface complexes is conditioned not only by the carbon substratum but also by the method used in their formation, in particular by the sulphurising agent and heat treatment temperature. In this study, activated carbon is subjected to different thermal and chemical treatments, using sulphurising agents like SO_2 and H_2S from the gas phase to modify its physical structure and/or the chemical nature of its surface. To assess the effectiveness of the treatments, the resultant products and the starting carbon have been used as adsorbents for cadmium from aqueous solution.

Needless to say, an important property for the sulphur complexes formed by heating carbon in a sulphurising atmosphere is their thermal stability, which is generally high [14]. Thus even outgassing the carbon at 1200 °C did not completely eliminate the sulphur, and there always remained an appreciable quantity of residual sulphur fixed to the surface of the carbon. Its total elimination required heating the carbon to 900 °C in the presence of a reducing hydrogen atmosphere.

2. Experimental

The adsorbents used here were a commercial Merck carbon (1.5 mm, C–S) and three samples prepared from it: treatment from ambient temperature to 900 °C in an SO_2 atmosphere (C–SO_2-900); at ambient temperature also only in SO_2 (C–SO_2–N_2-30); and successively in SO_2 and H_2S at ambient temperature (C–SO_2–H_2S–N_2-30). Specific conditions of the sulphurising treatments of C–S were as follows.

2.1. Treatment to 900 °C in SO_2

The SO_2 treatment was performed by passing a stream of this gas at a constant flow rate of 50 ml min^{-1} through approximately 5 g of C–S in a quartz reactor. Before heating, the

Table 1
Ultimate analysis of the samples (wt.%)

Sample	C	H	N	S	O
C–S	83.6	0.9	1.1	0.1	14.3
C–SO$_2$-900	44.5	1.3	0.7	17.2	36.3
C–SO$_2$–N$_2$-30	70.9	0.8	1.0	2.7	24.6
C–SO$_2$–H$_2$S–N$_2$-30	75.4	0.7	1.1	14.7	8.1

air initially present in the reactor was flushed out by passing the SO$_2$ current for 30 min. The system was then heated at a rate of 5 °C min^{-1} from 30 to 900 °C. The SO$_2$ gas was produced by reacting Na$_2$S$_2$O$_5$ (sodium metabisulphite) with H$_2$SO$_4$ (sulphuric acid).

2.2. Treatment at 30 °C in SO$_2$ and transport with N$_2$

Approximately, 5 g of carbon was placed in the reactor inside an oven at 30 °C and soaked with SO$_2$ stream (flow rate = 50 ml min^{-1}) for 110 min. After that, the sulphurising stream was replaced by another one of N$_2$ (purity = 99.998%, flow rate = 100 ml min^{-1}) which, with the oven at the same temperature, was maintained during an identical time.

2.3. Successive treatment at 30 °C in SO$_2$ and H$_2$S and transport with N$_2$

As with the previous cases, approximately 5 g of carbon was used, performing the treatment at 30 °C in two successive steps with SO$_2$ (flow rate = 50 ml min^{-1}) for 110 min and with H$_2$S (flow rate = 50 ml min^{-1}) for 60 min; transport with N$_2$ (purity = 99.998%, flow rate = 100 ml min^{-1}) was carried out for 100 min.

2.4. Characterisation of the samples

The data of the chemical analysis of the samples are given in Tables 1 and 2. The ultimate analysis (C, H, N) was performed using a Perkin-Elmer model 240 C analyser. The sulphur content of C–S was determined using a LECO device, in which the sample is burnt and the resultant gas is analysed by FT-IR spectroscopy or thermal conductivity. For the rest of the samples, which had high sulphur contents, the Eschka method was used (standard analysis, UNE 32008). It deals with the transformation into BaSO$_4$ of the sulphur present in the sample by treatment first with the Eschka mixture (MgO, Na$_2$CO$_3$) at 800 °C and then

Table 2
Proximate analysis of the samples (wt.%)

Sample	Moisture	Volatile matter	Fixed carbon	Ash
C–S	10.9	7.2	80.3	1.6
C–SO$_2$-900	17.4	27.6	51.1	3.9
C–SO$_2$–N$_2$-30	14.5	14.6	69.6	1.3
C–SO$_2$–H$_2$S–N$_2$-30	5.7	24.7	68.3	1.3

successively with aqueous solutions of Br_2 and $BaCl_2$. The oxygen content was obtained by difference.

The proximate analysis (moisture, volatile matter, ash) of the samples was carried out using a thermogravimetric method [15]. It consists of heating (rate $= 80\,^\circ C\,min^{-1}$) the sample from 30 to $950\,^\circ C$ in N_2 and of the subsequent combustion of the pyrolysed residue in O_2. The fixed carbon content was estimated by subtraction.

The changes produced in the surface area and the microporosity of C–S as a result of the sulphurising treatments were investigated by physical adsorption of N_2 at $-196\,^\circ C$. The adsorption isotherms were determined using a conventional gravimetric device. Prior to the adsorption measurements, the adsorbents were first oven dried at $110\,^\circ C$ for 24 h and then outgassed at $150\,^\circ C$, at a pressure of 133×10^{-6} Pa. The equilibration time for each isotherm point was lower than 4 h.

2.5. *Adsorption of Cd^{2+} from aqueous solution*

In the study of the adsorption of Cd^{2+} from aqueous solution, the concentration of an Cd^{2+} solution in contact with the each adsorbent was monitored first as a function of time between a few minutes and 200 h. In this way, it was possible to know the rough time needed for each individual adsorption system to reach equilibration. To such an end, in a Selecta thermostatic shakerbath, containing water at 25 or $45\,^\circ C$, was placed a series of 250 ml glass flasks (provided with Bakelite screw-on caps to prevent solvent losses by evaporation) each with approximately 0.1 g of carbon to which was added 100 ml of 0.5 mM solution of Cd^{2+} at either the unmodified Cd^{2+} solution pH at 6.2 or at 2.0 (this pH value was chosen at random to have an idea of the effect of the change in the surface charge of the samples on the adsorption of Cd^{2+}). Then, the adsorption isotherms of Cd^{2+} were measured, using approximately 0.11 g of adsorbent and 50 ml of Cd^{2+} solution of known concentration in the range 9.9×10^{-2} to 7.6 mM. After equilibration (for safety's sake, as usual, much longer was given to all systems; thus, regarding the adsorption at 25 or $45\,^\circ C$ and pH 6.2, time was approximately 15 h for C–S, 80 h for C–SO_2-900 and C–SO_2–H_2S–N_2-30, and 40 h for C–SO_2–N_2-30; at pH 2.0 such a time was even higher), the supernatant liquid was assayed by atomic absorption spectophotometry, using a Perkin-Elmer model 370 apparatus. The cadmium salt used in the preparation of the aqueous solutions of Cd^{2+} was $CdCl_2 \cdot H_2O$ (analytical reagent, Merck).

3. Results and discussion

As shown in Table 1, the treatment of C–S between 30 and $900\,^\circ C$ in SO_2 greatly decreased the carbon content and increased the contents of sulphur and oxygen. The reaction of SO_2 with carbons has been thoroughly studied at different temperatures. As reported earlier when investigating the thermogravimetric behaviour of C–S in SO_2 [7], between 510 and $710\,^\circ C$ the considerable weight gain of 4.7 wt.% occurred. The mass increase at temperatures of this order was associated with the deposition of elemental sulphur [16] and with the formation of sulphur surface complexes with the possible chemisorption of sulphur dioxide and oxygen [12,17] on carbon surfaces. The fixation of surface sulphur mainly as

polymerised sulphur, held in the micropores, was also suggested [18]. However, at higher temperatures between 710 and 900 °C there was a mass loss of 16.0 wt.% [7]. This variation of the mass was attributed to the removal of surface sulphur and sulphur complexes and to the partial gasification of the carbon. Gas composition depended on heat treatment temperature [19]. Thus, at 700 °C species like COS, CO_2, S, and traces of CS were formed, whereas above 900 °C the main products were CO and monoatomic sulphur [20].

When the treatment of C–S in SO_2 was effected at 30 °C, it also resulted in a decrease in the carbon content and in an increase in the contents of sulphur and oxygen (Table 1). However, as expected, the changes produced in the elementary composition of C–S were less strong than when heating to 900 °C. Thus, the increase in the sulphur content was much lower (i.e., 2.7 wt.%) for C–SO_2–N_2-30 than for C–SO_2-900. It contrasted with the great mass gain produced at 30 °C, which was as high as 43.0 wt.% after soaking for 110 min in SO_2 [7]. Although it should also be noted that the mass loss produced in the subsequent contact of the intermediate SO_2-treated product with N_2 amounted to ≈27.0 wt.% [7]. These two figures indicated that a great part of the surface species present in the SO_2-treated product was weakly fastened, and hence easily removed by transport with N_2.

Comparison of the sulphur contents for C–SO_2–N_2-30 and C–SO_2–H_2S–N_2-30 denoted that sulphur surface species arising from the treatment of C–S at 30 °C in SO_2 stabilised when the resultant intermediate product was further treated with H_2S prior to the contact with the N_2 stream. The stabilisation of surface sulphur was likely connected with the occurrence of the following reaction

$$SO_2 \text{ (surface)} + 2H_2S \text{ (g)} \rightarrow S_8 \text{ (surface)} + 2H_2O \text{ (l)}$$
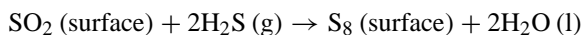
between adsorbed and/or chemisorbed SO_2 and H_2S (g), which was compatible not only with the higher sulphur content of C–SO_2–H_2S–N_2-30 than of C–SO_2–N_2-30 but also with the lower oxygen content for the former product.

Table 2 shows that the moisture content of the different samples varied between 5.7 and 17.4 wt.%. The high moisture content for C–S (i.e., 10.9 wt.%) was coherent with the great adsorption capacity of activated carbons. For the sulphurised samples, the amount of adsorbed water was notably affected by the existence of basic atoms able to form hydrogen bonds with water molecules. This was why the moisture content was higher in the SO_2-treated samples (and maximal in C–SO_2-900), in which there may also occur the solution of SO_2 and the partial reaction of dissolved SO_2 with carbon surface functional groups. In fact, SO_2 gas dissolved fairly readily in water; at 15 °C, 45 vol. SO_2 in 1 vol. water. In the case of C–SO_2–H_2S–N_2-30, in the preparation of which H_2S acted as the reducing agent, there was a decrease in the number of groups or molecules containing oxygen atoms, so less water would be retained.

The ash content was low for C–S, as was usually recommended for activated carbons used in the adsorption of solutes from aqueous solution. The changes produced in the ash content of the sulphurised samples as compared to C–S were simply attributed to relative variations in the contents of moisture, volatile matter, and fixed carbon. In the case of C–SO_2-900, for instance, the significant increase in the ash content was likely mainly associated with the great decrease in the fixed carbon content. Changes in the chemical composition of the inorganic fraction of C–S were not expected to occur for the samples

Table 3
Values of S_{BET} and W_0

Sample	S_{BET} ($m^2 g^{-1}$)	W_0 ($cm^3 g^{-1}$)
C–S	921	0.40
C–SO$_2$-900	831	0.35
C–SO$_2$–N$_2$-30	890	0.39
C–SO$_2$–H$_2$S–N$_2$-30	842	0.36

prepared at room temperature, at least, as a result of the sulphurising treatments of the material. For C–SO$_2$-900, however, it would depend on a number of factors as maximum heat treatment temperature in the preparation of C–S relative to 900 °C, the effect of SO$_2$ atmosphere, and so on.

The higher contents of volatile matter together with the lower contents of fixed carbon for the three sulphurised samples than for C–S again proved the effectiveness of the methods used in this study to introduce sulphur into the carbon (cf. the sulphur values are given in Table 1). Notice that the content of volatile matter was significantly higher for C–SO$_2$-900 and C–SO$_2$–H$_2$S–N$_2$-30 than for C–SO$_2$–N$_2$-30. In connection with the thermal behaviour of the surface state for the sulphurised samples it should be noted that the DTG curves showed the presence of two or three maximums of weight loss centred at temperatures lower than 500 °C [7].

The values of S_{BET} and W_0 (Table 3; S_{BET} was the specific surface area, as obtained from the N$_2$ adsorption isotherms at −196 °C by applying the Brunauer et al. equation [21] in the relative pressure range between 0.05 and 0.35, and taking the average area occupied by a molecule of N$_2$ in the completed monolayer to be equal to 16.2 Å^2; W_0 was the micropore volume, expressed as liquid volume, derived from the application of the Dubinin–Radushkevich equation [22] to such isotherms) are given in Table 3. S_{BET} and W_0 were notably lower for C–SO$_2$-900 and C–SO$_2$–H$_2$S–N$_2$-30 than for C–S. Accordingly, the reduction of surface area and microporosity was more important for such a couple of samples, which possessed a higher sulphur content. For C–SO$_2$–N$_2$-30, the unfavourable effect on S_{BET} and W_0 was of less significance. For C–SO$_2$–N$_2$-30 and C–SO$_2$–H$_2$S–N$_2$-30, which were both prepared at ambient temperature, the effect of porosity loss was attributable to stable sulphur species that should remain in the samples after outgassing in the adsorption apparatus. For C–SO$_2$-900, in addition, the gasification of pore walls likely contributed to the porosity decrease.

3.1. Adsorption in solution

The plots of solution concentration (C, mmol l^{-1}) for Cd^{2+} against time (t, h) for the various adsorbents (Figs. 1–3) show that, irrespective of adsorption temperature, equilibration in the adsorption system was reached before 25 h. Furthermore, the introduction of sulphur species into the carbon hardly had an unfavourable effect on the process kinetics. Such an effect was only somewhat stronger when the Cd^{2+} solution at pH 2.0 was used. In this case the equilibration time for the sulphurised samples was higher than 100 h, though the variation of C with t was not very significant above 50 h.
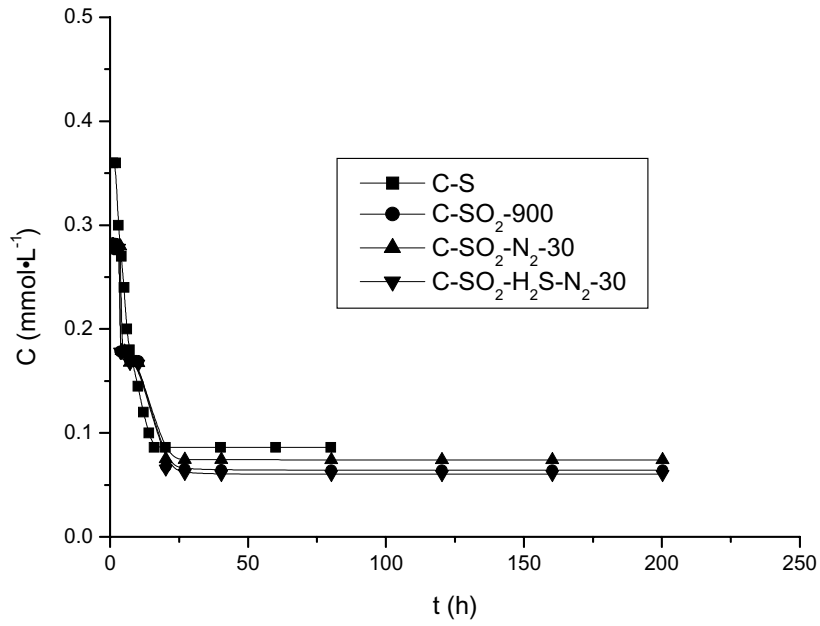
Fig. 1. Variation of concentration of the Cd^{2+} solution against time at $T = 25\,^{\circ}$C, pH = 6.2.
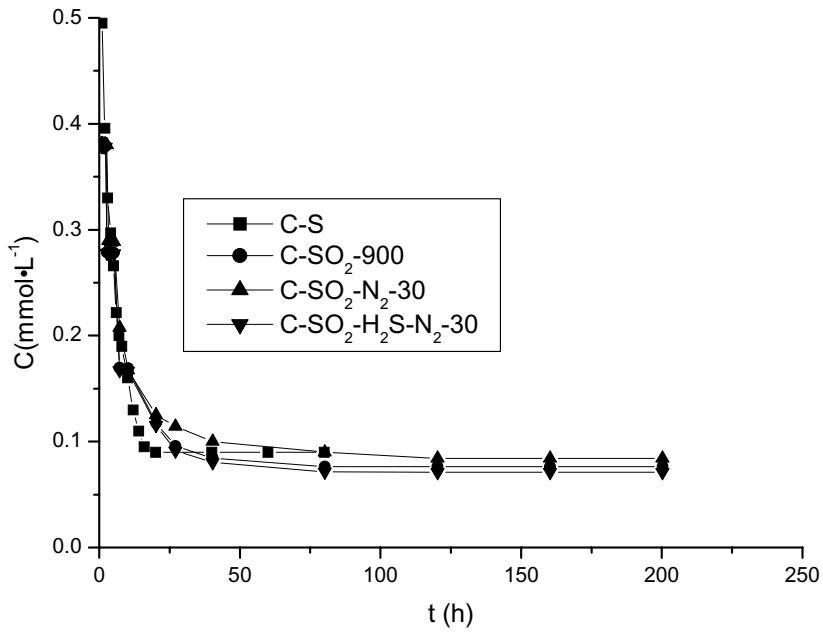

Fig. 2. Variation of concentration of the Cd^{2+} solution against time at $T = 25\,^{\circ}$C, pH = 2.0.
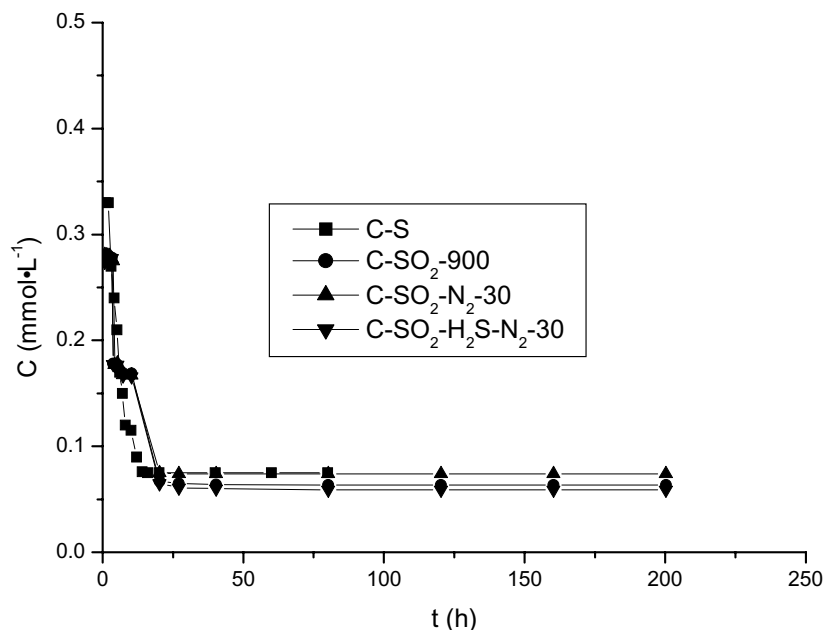
Fig. 3. Variation of concentration of the Cd^{2+} solution against time at $T = 45\,°C$, pH = 6.2.

The effectiveness of the sulphurising treatments in improving the adsorption capacity of the carbon for Cd^{2+} was evident simply from Figs. 4–6 as the isotherm for C–S was situated below the others. The adsorption of metallic ion was higher by the order: C–SO$_2$-900 > C–SO$_2$–H$_2$S–N$_2$-30 > C–SO$_2$–N$_2$-30 > C–S. As an example, the IPAA (Table 4) for the

Table 4
Comparison of the adsorption of Cd^{2+}[a]

Sample	Temperature (°C)/pH	AA	IPAA	VPAA
C–S	25/6.2	0.275		
C–SO$_2$-900	25/6.2	0.418	52.0	
C–SO$_2$–N$_2$-30	25/6.2	0.298	8.4	
C–SO$_2$–H$_2$S–N$_2$-30	25/6.2	0.390	41.8	
C–S	45/6.2	0.269		−2.2
C–SO$_2$-900	45/6.2	0.458	70.3	+9.6
C–SO$_2$–N$_2$-30	45/6.2	0.356	32.3	+19.5
C–SO$_2$–H$_2$S–N$_2$-30	45/6.2	0.424	57.6	+8.7
C–S	25/2.0	0.220		−20.0
C–SO$_2$-900	25/2.0	0.280	27.3	−33.0
C–SO$_2$–N$_2$-30	25/2.0	0.262	19.1	−12.1
C–SO$_2$–H$_2$S–N$_2$-30	25/2.0	0.262	19.1	−32.8

[a] AA: amount adsorbed of Cd^{2+} at the equilibrium concentration (C) of 4 mmol l^{-1}; IPAA: increase percentage in AA $= C_{sample} - C_{C–S}/C_{C–S} \times 100$; VPAA: variation percentage in AA $= C'' - C'/C' \times 100$, where C' and C'' being AA at 25 °C/pH 6.2 and 45 °C/pH 6.2 or 25 °C/pH 2.0, respectively, for a given adsorbent.

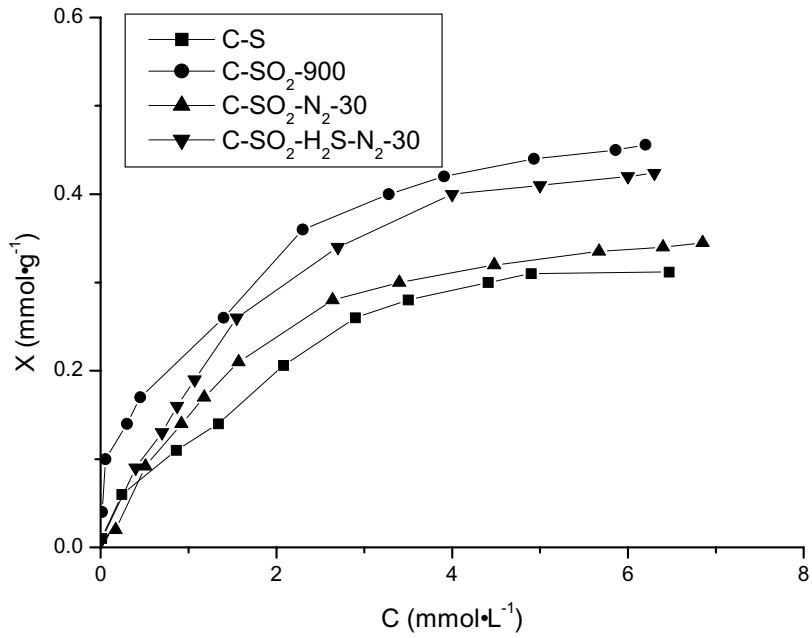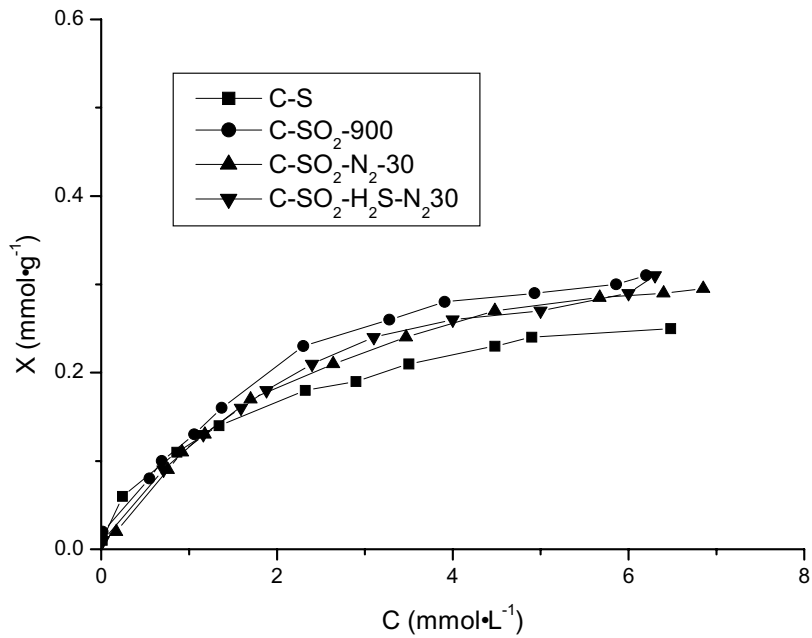Fig. 4. Adsorption isotherms for Cd^{2+} at $T = 25\,^{\circ}C$, pH $= 6.2$.

Fig. 5. Adsorption isotherms for Cd^{2+} at $T = 25\,^{\circ}C$, pH $= 2.0$.
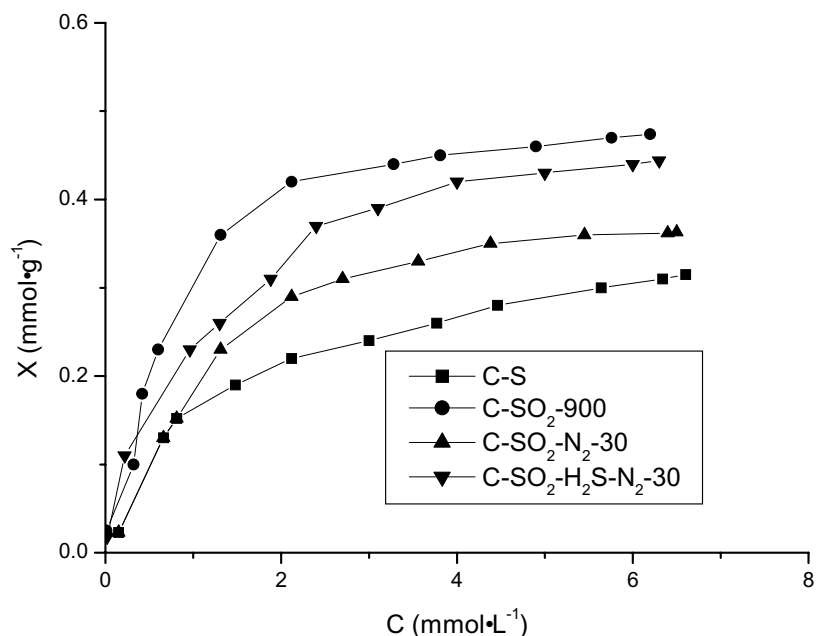
Fig. 6. Adsorption isotherms for Cd^{2+} at $T = 45\,^{\circ}C$, pH = 6.2.

adsorption at $25\,^{\circ}C$ and pH 6.2 was 52.0 for C–SO_2-900, 41.8 for C–SO_2–H_2S–N_2-30, and 8.4 for C–SO_2–N_2-30. The IPAA varied in the ranges: 8.4–52.0 ($25\,^{\circ}C$/pH 6.2), 32.3–70.3 ($45\,^{\circ}C$/pH 6.2), and 19.1–27.3 ($25\,^{\circ}C$/pH 2.0) for the sulphurised samples. Therefore, the influence of the sulphurising method of C–S was greater at pH 6.2, both at 25 and $45\,^{\circ}C$, than at pH 2.0.

The magnitude of the increase in the adsorption of Cd^{2+} not only depended on the sulphurising treatment effected to C–S but also on temperature and pH of the Cd^{2+} solution. Thus it was larger at $45\,^{\circ}C$ than at $25\,^{\circ}C$ (except for C–S) and also at pH 6.2 than at pH 2.0. The VPAA (Table 4) ranged between -2.2 and 19.5 at $45\,^{\circ}C$ and between -12.1 and -33.0 at pH 2.0.

As far as the adsorption of Cd^{2+} by C–S was concerned, it should occur on active centres of the carbon surface, possibly basic centres. Since the equilibrium times were short (i.e., 20 h at most for the adsorption at $25\,^{\circ}C$ and pH 2.0), one was led to think that this was a case of a relatively fast adsorption process (physical adsorption, probably with a contribution from chemisorption) in which the Cd^{2+} ions were fairly strongly attached to the active centres of the carbon [23].

The fact that the adsorption of Cd^{2+} was usually greater with increasing sulphur content of the samples proved that sulphur surface species took part in the uptake process. It should be taken into account that for C–SO_2-900 and C–SO_2–H_2S–N_2-30, which were the samples having the largest adsorption capacities to Cd^{2+}, there was a significant reduction in their surface area and porosity, and that this should detrimentally affect the extent of Cd^{2+} adsorption. On the other hand, since kinetics of the adsorption process was not very different

for C–S and the sulphurised samples (except, may be, for the adsorption at pH 2.0), in spite of the presence of surface sulphur in the latter products, it argued for a similar adsorption mechanism irrespective of whether the adsorbent contained such a sulphur or not. Perhaps, for the sulphurised products the adsorption of Cd^{2+} to a significant extent occurred on active sites present in C–S that were not affected by the sulphurising treatments (if so, the sulphur complexes were formed in other surface positions of C–S), and it markedly influenced the relatively fast kinetics of the process. Nevertheless, the increase in the adsorption of Cd^{2+} with the rise in temperature for the sulphurised samples was compatible with chemisorption of Cd^{2+} and also with a larger degree of diffusion of this metallic ion in pores of the adsorbents. Finally, the decreased adsorption at pH 2.0 denotes a strong competition effect between the proton and the metallic ion towards the active sites of the adsorbents.

4. Conclusions

From our results it can be concluded that the treatments of C–S in atmospheres of SO_2 or SO_2 and H_2S enabled us to modify chemico-physical properties of the material and hence its ability to adsorb Cd^{2+} from aqueous solution. The amount of sulphur introduced in C–S was larger when heating to 900 °C in SO_2 and smaller when sulphurising also in SO_2 but at ambient temperature. A correlation was noted between the amount of sulphur introduced in C–S and the loss of surface area and microporosity. The kinetics of the adsorption process of Cd^{2+} was not markedly affected as a result of the increased presence of sulphur in the samples. The adsorption capacity depended on the treatment effected to C–S and also on adsorption temperature and pH of the adsorptive solution. The most effective treatment was heating to 900 °C, the adsorption in this case being 70.3% more than that of the starting carbon. The adsorption increased at 45 °C but decreased at pH 2.0 when compared to adsorption at 25 °C and pH 6.2, respectively. In short, by sulphurising C–S it was possible to enhance the adsorption capacity of the material to Cd^{2+}, the detrimental effect on the kinetics of the process being of little significance.

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