POLLUTANTS REMOVAL ONTO NOVEL ACTIVATED CARBONS MADE FROM LIGNOCELLULOSIC PRECURSORS

J.M. Valente Nabais[1]*, C. Laginhas[1], P.J.M. Carrott[1], M.M. Ribeiro Carrott[1], J.A. Gomes[1], Suhas[1], A. Ramires[1], S. Roman[2]

[1]*Centro de Química de Évora & Dep. de Química, Univ. de Évora, Rua Romão Ramalho nº 59, 7000-671 Évora, Portugal*
[2]*Departamento de Física Aplicada, Universidad de Extremadura, 06071, Badajoz, Spain*

** Corresponding author. E-mail : jvn@uevora.pt*

Abstract. The adsorption of phenol and mercury from dilute aqueous solutions onto new activated carbons was studied. These included activated carbons produced from novel precursors, namely rapeseed, vine shoots and kenaf, and samples oxidised with nitric acid in liquid phase. The results have shown the significant potential of rapeseed, vine shoots and kenaf for the activated carbon production. The activated carbons produced by carbon dioxide activation were mainly microporous with BET apparent surface area up to $1224 m^2 g^{-1}$ and pore volume $0.5 cm^3 g^{-1}$. The effects of concentration and pH were studied. The phenol adsorption isotherms at 25ºC followed the Freundlich model with maximum adsorption capacities of approximately $80 mg g^{-1}$ and $60 mg g^{-1}$ for the pristine and oxidised activated carbons, respectively. The influence of pH on the phenol adsorption has two trends for pH smaller and bigger than 10. The maximum adsorption capacity of mercury adsorption onto activated carbon made from vine shoots reaches $1103 mg g^{-1}$. The adsorption depends on the mercury species and the on the adsorbent properties, namely porosity and net surface charge.

1. Introduction

Lignocellulosics (LCs) are widely used raw materials for activated carbon (AC) production with wood and coconut shell being the major precursors, and accounting for more than 165,000 ton/yr of AC production. However, the search for new precursors is needed in order to produce activated carbons from low cost materials, such as industrial and agricultural residues, with potential to be used in a number of applications, like pollutants removal, gas separation and storage and other industrial uses.

Phenol and mercury are two important toxic materials listed as priority pollutants by the US Environmental Protection Agency (EPA) and also by the EU. Phenol is considered to be very toxic to humans through oral exposure with symptoms including muscle weakness and tremors, loss of coordination, paralysis, convulsions, coma, liver and kidney damage, headache, fainting and other mental disturbances. The ingestion of 1g has been reported to be lethal. Inhalation and dermal exposure to phenol is highly irritating to the skin, eyes, and mucous membranes in humans. Mercury and its compounds act as dangerous and insidious poisons, with the possibility of adsorption not only through the gastrointestinal tract but also through the skin and lungs. After adsorption, mercury circulates in the blood and is stored in the liver, kidneys, brain, spleen and bone, thereby leading to several health problems such as paralysis, serious intestinal and urinary complications, dysfunction of the central nervous system and, in more severe cases of intoxication, death. The soluble compounds of mercury are particularly toxic because their adsorption is very fast. Ingesting a dose of less than 0.5 g can prove to be fatal.

The high toxicity leads to very restrictive legislation regarding the permitted discharge. For example the 80/778/EEC directive of the European Commission states a maximum admissible concentration of 0.5 $\mu g l^{-1}$ for phenol in water intended for human consumption. For mercury in the United States of America, the permitted discharge limit of wastewater for total mercury is 10g/l and the limit for drinking water is 2g/l. The World Health Organization (WHO) recommends a maximum uptake of 0.3 mg per week and 1g/l as the maximum acceptable concentration of mercury in drinking water.

The increasing necessity for the reduction of phenol and mercury discharges and the removal of the pollutants from wastewaters before the transport and re-cycling of the latter into the environment requires the need for research and development of better methodologies that can provide effective and total removal from liquid effluents. The use of activated carbons can be considered a cost-effective method and seems to have an

advantage over the others available methods thanks to the higher removal efficiency and the flexibility of the industrial unit operation.

In general the uptake of an adsorbate (e.g. phenol and mercury) from aqueous solutions by ACs depends on various factors which include type of precursor for AC production, physical nature (surface area, pore size, pore volume, ash content, particle size) and functional groups present on the adsorbent, nature of adsorbate (pKa, polarity, molecular weight, size, solubility) and on adsorbate solution conditions (pH, concentration, temperature). The adsorption mechanism depends on a complex set of factors related to physical adsorption processes and specific interactions. These are determined by the porosity of the adsorbent and the size of the adsorptive molecules, and also by the requirement for both electrostatic and dispersive interactions to take place, either in conjunction or separately [1]. Specific interactions with surface groups are also possible, leading to the formation of complexes [2-4]. The most relevant factors affecting the adsorption of inorganic species are those which depend on the surface chemistry of the carbon material and the species to be adsorbed. In turn, these two features depend on the solution pH and also, for mercury, on the solution pCl [5, 6]. The adsorption mechanisms are not as yet fully understood and more research in the area is still needed to increase the knowledge about the relevant factors. Also, the development of better materials is still required. These were the main motivations behind the work now reported.

2. Experimental Methods

The activated carbon samples were produced from three lignocellulosic precursors, kenaf (*Hibiscus cannabinus)*, vine shoots *(vitis vinifera*) and rapeseed (*Brassica napus)*. The physical activation with carbon dioxide as activating agent was done in a horizontal tubular furnace with heating rate of 10ºC min^{-1}. Carbonisation was carried out for 1h by heating to 400ºC under a constant N_2 flow of 85cm^3min^{-1}. Activation was carried out at 700ºC under a CO_2 flow of 85cm^3min^{-1}, for different times in order to obtain several burn-offs, indicated in the samples designation after C7, V8 or K7, respectively, for activated carbon from rapeseed, vine shoots or kenaf, switching back to the N_2 flow and allowing to cool below 50ºC before removing the AC from the furnace. The vine shoots were activated at 800ºC using the same procedure. Samples K748, V840 and C738 were oxidised in liquid phase with concentrated nitric acid during 1 hour in a hot plate with stirring at 80-90ºC. The ACs were removed and washed with distilled water until the wash water attained the same pH value as the distilled water employed in the wash. The oxidised samples were designated as C738Ox, V840Ox and K748Ox.

Nitrogen adsorption isotherms at 77K were determined using a CE Instruments Sorptomatic 1990 after outgassing the samples at 400ºC to a residual vacuum of $5x10^{-6}$mbar. The point of zero charge was determined by mass titrations using three suspensions with 7%(w/v) in carbon material with initial pH of 3, 6, and 11; the three initial pH values were obtained by adjusting the pH of a solution $NaNO_3$ 0.1M with NaOH or HNO_3 solutions, more details given elsewhere [7]. A $1x10^{-2}$M phenol stock solution was prepared from phenol (>99%, Aldrich). Batch adsorption experiments were carried out in test tubes of 50cm^3 covered with rubber stoppers inserted into a shaking thermostat bath for 7 days. Each test tube contained 0.01g of AC and 10cm^3 of an appropriated phenol solution. The effects of concentration (0.1– 2mM) and pH (3-13) were studied. The quantification of the phenol in the liquid phase was carried out using a Thermo UV-Vis spectrophotometer at 270nm. An adsorbate stock solution containing 1500mg/l Hg(II) was prepared from $HgCl_2$. This solution was diluted to obtain the necessary concentrations for adsorption experiments. Batch adsorption experiments were carried out in a series of Erlenmeyer flasks of 100 ml capacity covered with Teflon sheets inserted into a shaking thermostat bath for 24h. Each flask contained 0.1g of fibres and 50ml of an appropriate Hg(II) solution. The effect of concentration (10–1500mg/l) was studied. Three different Hg(II) species were studied by controlling the chloride concentration at pCl=0 for $[HgCl_4]^{2-}$, pCl=4 for $HgCl_2$ and pCl=7 for Hg^{2+}. In the later case, the stock solution was prepared from $Hg(NO_3)_2.H_2O$. The total concentration of Hg(II) was determined by ultraviolet spectrophotometry from the absorbance arising from the tetrachloromercury(II) complex at 230nm.

The procedure involved adjusting the pCl to zero prior to the absorbance determination in order to transform all the Hg(II) present into the corresponding complex. Measurement details have been given previously [5].

3. Results and Discussion

The textural and chemical characterisation of the activated carbons produced from the lignocellulosic precursors can be seen in table 1. All pristine ACs have basic properties with pzc values between 9.63 and 9.98. The point of zero charge (pzc) is defined by the pH value at which the total surface charge is zero and gives an estimative of the material basicity/acidity.

The porous development of the produced ACs is very interesting. As shown in table 1 the apparent BET surface area reaches the maximum value of 1112, 1173 and 1021 m^2g^{-1} for rapeseed, vine shoots and kenaf samples, respectively. The ACs samples have a low to moderate external area (A_{ext}), given by the α_s method. All samples are microporous, as indicated by the shape of the nitrogen adsorption isotherms at 77K (not shown here for simplicity) which are all type I according to the IUPAC classification [8]. The difference between the pore volumes given by the α_s and Dubinin-Radushkevich (DR) methods, V_s and V_o, respectively, can provide an estimate of the primary and secondary micropore volume considering the α_s volume as the total pore volume and the DR pore volume as an indication of the primary micropores. As shown in table 1, all samples have very similar or equal values for both volumes which indicate that most of the pores present in the ACs samples are narrow micropores. The sample modification by liquid phase oxidation with nitric acid, samples C738Ox, V840Ox and K748Ox, had produced drastic alterations to the surface chemistry of the samples, as indicated by the pzc values that changed from 9.63 to 2.32, from 9.71 to 2.10 and from 9.98 to 2.05 for samples C738, V840 and K748, respectively. The impact of the nitric acid treatment on the porosity was much less noticeable. It caused a slightly decrease in the apparent BET surface area and pore volume. As can be seen in table 1, the apparent BET surface area decreased by approximately 25 and 15% for C738/V840 and K748, respectively. The decrease in pore volume was bigger for V840 and C738 than for K748. The results show that ACs from kenaf is more resistant to nitric acid treatment in liquid phase in regard to the sample pore properties. It seems that for K748 the nitric acid treatment undertaken results in a more extensive depletion of the materials external area with much less impact on their pore structure. Nevertheless, we can state that the main goal of the nitric acid treatment carried out, to produce samples with very different surface chemistry but similar pore structure, was fully achieved.

Table 1. Textural and chemical characterisation of the activated carbons

Sample	Porosity				pzc
	BET	α_S		DR	
	A_{BET} (m^2g^{-1})	V_s (cm^3g^{-1})	A_{ext} (m^2g^{-1})	V_0 (cm^3g^{-1})	
C738	1112	0.52	126	0.47	9.63
C738Ox	827	0.35	78	0.35	2.32
K748	1021	0.45	84	0.45	9.98
K748Ox	962	0.45	20	0.41	2.05
V840	856	0.44	26	0.40	9.71
V870	1173	0.53	31	0.47	9.84
V840Ox	646	0.29	41	0.25	2.10

For the study of the phenol adsorption from dilute aqueous solutions we selected four samples, C738, C738Ox, K748 and K748Ox, from different precursors and with different surface properties to evaluate the potential of the produced ACs to be used for the phenol removal and to understand the influence of the surface characteristics on the adsorption process. The mercury uptake was tested in three samples, V840, V870 and V840Ox. The solution chemistry is crucial to understand the adsorption mechanism of the inorganic species. Phenol can be considered as a weak acid with a pK_a value of 9.95. For pH values below the pK_a value the predominant specie in solution is the molecular form of phenol. For pH above this value the aromatic ring becomes partially negatively charged by means of the hydroxyl group ionisation. In consequence, the ionic form is predominant for pH values higher than 9.95. The predominance diagram for the Hg(II) species present under the experimental conditions employed is shown in Figure 1 [6, 9]. This diagram shows that it is possible to control the solution in order to ensure that positive, neutral or negative species, i.e. Hg^{2+}, $HgCl_2$ or $[HgCl_4]^{2-}$, respectively, predominate. It should be noted that the diagram depicted in Fig. 1 only considers the aqueous Hg(II) species and their homogeneous equilibria. However, the equilibria are modified when activated carbon are present. In particular, the solubility equilibrium is modified because the solubility of Hg(II) oxide or hydroxide increases as a consequence of mercury adsorption by the ACs. This causes the diagonal line in the diagram which indicates the start of precipitation to move to the right. Also, the presence of any type of precipitate was not observed, probably because of the increased solubility by the presence of the ACs already referred to and/or the adsorption of colloidal precipitate particles by the surface and pores of the ACs.

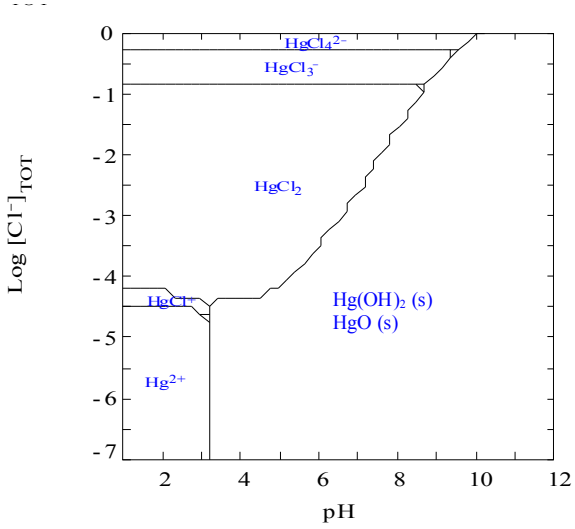

Fig. 1. Predominance diagram of mercury species established using MEDUSA® software [9]

The mercury uptake by the ACs produced from vine shoots can be seen in table 2. This table also shows the influence of the experimental conditions to the mercury adsorption, namely the solution pH and the ACs net surface charge. In adsorption processes the surface of the carbon materials can be positive, neutral or negatively charged depending on the pH at which the adsorption takes place. If the adsorption pH is equal to pzc the surface will be neutral, but if the adsorption pH is greater than the pzc the surface is positively charged. On the other hand, if the pzc is greater than the pH of the suspensions used in the adsorption process the surface is negatively charged. The charge of the surface can be important for understanding the adsorption of ionic species. The molecular/ionic dimension is also of great relevancy to the adsorption as it can constitute a barrier to the adsorption. For the mercury species the molecular/ionic dimensions are as follow: $Hg^{2+} < HgCl_2 < [HgCl_4]^{2-}$. As can be seen in table 2, the uptake of Hg^{2+} was greater than $[HgCl_4]^{2-}$ and $HgCl_2$ in all cases.

For each AC the mercury adsorption capacity shows the trend: Hg^{2+} > $HgCl_2$ > $[HgCl_4]^{2-}$, the observed behaviour is independent of the electrostatic interactions between the mercury species and the surface net charge. For instance, if we compare the adsorption of $[HgCl_4]^{2-}$ and Hg^{2+} onto V840 or V870 we can observe that, despite having more favourable electrostatic interactions, the negatively charged species always have smaller adsorption onto ACs samples. This indicates that the possible effect of electrostatic interactions is not relevant in this case being the molecular/ionic dimensions and the porosity of the samples the critical factors to the mercury uptake. The only exception is the adsorption of Hg^{2+} onto V840Ox where the electrostatic attraction can have a positive influence on the mercury uptake. In this case, the maximum adsorption capacity increases despite the decrease of the apparent BET surface area and of the pore volume. This behaviour is opposite to the performance of samples V840 and V870.

The Hg(II) maximum adsorption capacity shown by ACs made form vine shoots can be favourable compared to other published results. Lopez-Gonzalez et al. [10] studied the influence of functional groups and the suspension pH in the mercury adsorption by three commercial activated carbons and reported the value 200mg/g as the highest value obtained. Namasivayam and Kadirvelu [11] reported an adsorption capacity of 154mg/g at pH 5 for activated carbons from coirpith. Ekinci et al. [12] using pH 5.5 and suspensions of 10mg Hg/50mL reported the value 160mg/g. Other examples of reported values are 28.4mg/g [13], 362.2mg/g [14] and 60mg/g [4]. Nevertheless, the above comparison must be considered only as an approximation because in some cases neither the predominance nor the speciation diagram were shown in the published papers nor did they refer to which Hg(II) species were present in aqueous solution nor the degree of ionisation of the surface functional groups. Again, in some other cases, the experimental conditions were somewhat different from ours, which can lead to misleading comparisons.

Table 2 Adsorption conditions and mercury maximum adsorption capacity

Hg(II) species	AC sample	pzc	$pH_{initial}$	Net surface charge	Maximum adsorption capacity / mgg^{-1}
	V840	9.71		+	190
$[HgCl_4]^{2-}$	V840Ox	2.10	6	-	89
	V870	9.84		+	203
	V840	9.71		+	515
$HgCl_2$	V840Ox	2.10	5	-	103
	V870	9.84		+	583
	V840	9.71		+	710
Hg^{2+}	V840Ox	2.10	3	-	1103
	V870	9.84		+	895

The phenol adsorption capacity for the pristine and oxidised activated carbons can be observed in table 3. The comparison of our results with results already published shows that the performance of the activated carbons tested can be considered very good. Stavropoulos *et al.* [15] and Singh *et al.* [16] reported phenol adsorption up to $35mgg^{-1}$. Din *et al.* [17] and Villacañas *et al.* [18] published slightly higher values, between 60 and $150mgg^{-1}$.

As can be seen in table 3 the oxidised samples have much less adsorption capacity when compared with the pristine sample. The lower adsorption capacity of the oxidised samples can not be explained only by the porosity

modification of the samples. The performance of the oxidized samples can be attributed to two different reasons. On one hand for the oxidised samples it is more difficult to displace the solvent molecules (water) from the AC surface in order to adsorb phenol due to the possibility of hydrogen bond formation between the surface oxygen groups and the water molecules. On the other hand, the functionalisation of the AC surface by nitric acid oxidation lead to a smaller electronic density of the basal planes, which are accessible to phenol adsorption, due to a stronger localisation of the π electrons at the ACs graphene layers. When phenol is predominantly in the molecular form the adsorption occurs mainly via the π-π dispersion interaction between the π delocalised electrons on the ACs graphene layers and the aromatic ring of the phenol molecule. Therefore, the increase in oxygen content, included in the oxygenated surface functional groups, leads to a decrease in this interaction as it tends to localise the π electrons of the graphene layers.

Table 3 Adsorption conditions and phenol maximum adsorption capacity

Sample	pzc	pK_a (phenol)	$pH_{initial}$	Phenol	Net surface charge	Phenol adsorption maximum / mgg^{-1}
C738	9.63				~0	84.1
C738Ox	2.32	9.95	7.5	molecular	-	57.0
K748	9.98				~0	82.6
K748Ox	2.05				-	63.1

The study of the influence of initial solution pH on the phenol adsorption can be seen in fig. 2. The vertical lines correspond to the pzc of the carbons and designate the turning point of the ACs mean surface charge. For pH values situated on the left side and on the right side of the lines the ACs have positive and negative charge, respectively. The increasing distance from the vertical lines corresponds to surfaces with greater charge density, as the difference between the pH and pzc values is also bigger. The phenol ionisation curve is also inserted in fig. 2.

As can be seen in fig. 2 the phenol adsorption decreases with pH. We can observe two distinct areas or behaviour, the first one for pH values less than 10 where the phenol removal only shows a slight decrease. The second trend is observed for pH values higher than 10 with the occurrence of a noteworthy decrease in the phenol removal. The same trend was also observed by Hameed and Rahman [19].

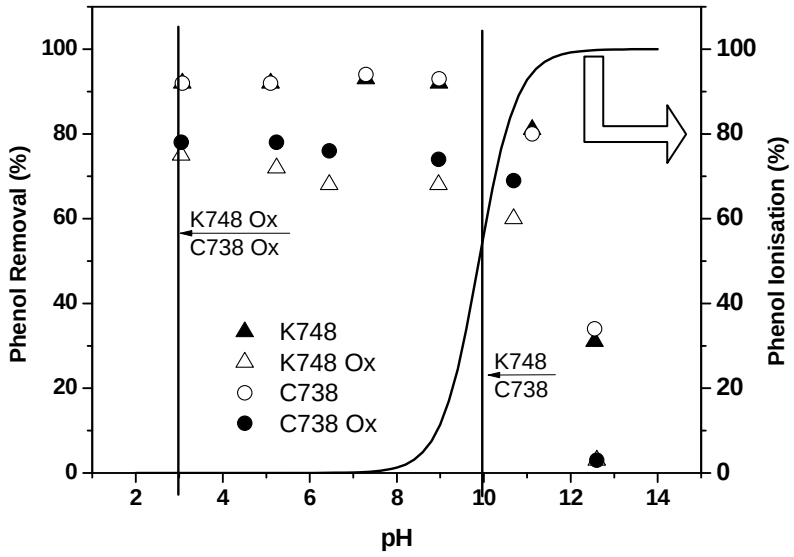

Fig. 2 Phenol removal as function of the initial solution pH [20].

For pH below 10 phenol is predominately in the molecular form and thus the electrostatic interactions do not have a significant role on the adsorption. That is why we can not observe, with the pH increase from 3 to 10, a higher decrease in the adsorption for samples C738Ox and K748Ox, which have a negatively charged surface or a increase in the adsorption for samples C738 and K748, which have a positive surface charge. In this zone the driving force for the adsorption is the dispersive interactions which are not determined by the electric nature of the surface. The oxidised samples have smaller adsorption capacity due to the effect of the oxide functional groups inserted on the ACs surface. For pH above 10 the phenolate ion became the predominant species in solution and hence the electrostatic repulsion between the phenolate and the negatively charged ACs surface leads to a significant decrease in the phenol adsorption. This decrease is more relevant for samples C738Ox and K748Ox as these samples have a higher charge density caused by a more extensive ionisation of the functional groups indicated by the bigger difference between solution pH and the ACs point of zero charge.

4. Conclusion

As conclusions we would like to focus three different topics:

1) Activated carbon production from new precursors

The use of rapeseed, vine shoots and kenaf as precursors for activated carbon production is very motivating. All activated carbons produced in this study have basic properties with point of zero charge values higher than 9 and a well developed porous structure. For instance, the apparent BET surface area reaches the maximum value of 1112, 1173 and 1021 m^2g^{-1} for rapeseed, vine shoots and kenaf samples, respectively.

2) Phenol removal

The phenol adsorption at 25ºC reveals that oxidised samples have much less adsorption capacity than the corresponding pristine activated carbon because the increased acidity of oxidised samples leads to an intensity decrease in the adsorption driving force, which is based on the π-π dispersion interaction between the π delocalised electrons on the activated carbon graphene layers and the aromatic ring of the phenol molecule. The phenol adsorption for pH less than 10 is independent of the solution pH. On the other hand, for pH values higher than 10 a noteworthy decrease in the phenol removal was observed. Therefore, we can conclude that phenol adsorption occurs via two possible mechanisms being the first one attributed to the adsorption by means of dispersive interactions between the phenol aromatic ring and the activated carbon aromatic structure. In this case the electrostatic interactions don't have a significant role on the adsorption. The second mechanism, which is based on the dispersive attractive forces and the electrostatic repulsion interactions, occurs when phenol is predominantly in the phenolate form and the activated carbon surface is negatively charged.

3) Mercury removal

The uptake of Hg^{2+} was greater than $[HgCl_4]^{2-}$ and $HgCl_2$ in all cases. The maximum adsorption capacity for each species was 1103, 203 and 583mgg^{-1}, respectively. These values compare quite well with other results published for this system. Sample V870 appeared to the best for the adsorption of $[HgCl_4]^{2-}$ and $HgCl_2$, whereas sample V840Ox was best for the adsorption of Hg^{2+}. The results also indicates that the possible effect of electrostatic interactions is not relevant for the adsorption process and also that the molecular/ionic dimensions and the porosity of the samples are the critical factors to the mercury uptake.

Finally we would like to conclude that activated carbons from rapeseed, vine shoots and kenaf are promising materials to be used for contaminated water treatment as the obtained results can be favourably compared with other reported papers. We would like to mention that this is an ongoing work. We will continue the work by testing the phenol and mercury adsorption on all ACs samples in order to better understand the adsorption mechanisms, in particular the influence of the basal planes and specific interactions with the functional groups present in the material surface.

Acknowledgements

The authors are grateful to the Fundação para a Ciência e Tecnologia (Portugal) and the European Regional Development Fund (FEDER) for financial support (Project PTDC/CTM/66552/2006).

References

[1] L.R. Radovic, C. Moreno-Castilla, J. Rivera-Ultrilla, *Chem. Phys. Carbon* **27** (2000) 228.
[2] J. Goel, K. Kadirvelu, C. Rajagopal, V.K. Garg, *Carbon* **43** (2005) 197-200.
[3] M.F. Yardim, T. Budinova, E. Ekinci, N. Petrov, M. Razvigorova, V. Minkova, *Chemosphere* **52** (2003) 835-841.
[4] K. Kadirvelu, M. Kavipriya, C. Karthika, N. Vennilamani, S. Pattabhi, *Carbon* **42** (2004) 745-752.
[5] P.J.M. Carrott, M.M.L. Ribeiro Carrott, J.M.V. Nabais, *Carbon* **36** (1998) 11-17.
[6] J.M. Valente Nabais, P.J.M. Carrott, M.M.L. Ribeiro Carrott, M. Belchior, D. Boavida, T. Diall, I. Gulyurtlu *Appl. Surf. Sci.* **252** (2006) 6046-6052.
[7] P.J.M. Carrott, J.M.V. Nabais, M.M.L. Ribeiro Carrott, J.A. Menendez, *Micr. Mesop. Mat.* **47** (2001) 243-252.
[8] J. Rouquerol, D. Avnir, C.W. Fairbridge, D.H. Everett, J.H. Haynes, N. Pernicone, J. Ramsay, K.S. Sing, K.K. Unger, *Pure and Applied Chemistry* **66 (8)** (1994) 1739–1758.
[9] J.M. Valente Nabais, P.J.M. Carrott, M.M.L. Ribeiro Carrott, S. Silvestre, C.J. Durán-Valle, *Adsoprtion Sci. Technol.* **25(3-4)** (2007) 199-215.
[10] J.D. Lopez-Gonzalez, C. Moreno-Castilla, A. Guerrero-Ruiz, F. Rodrıguez-Reinoso, *J. Chem. Tech. Biotechnol.* **32** (1982) 575-579.
[11] C. Namasivayam, K. Kadirvelu, *Carbon* **37** (1999) 79-84.
[12] E. Ekinci, T. Budinova, F. Yardim, N. Petrov, M. Razvigorova, V. Minkova, *Fuel Process. Technol.* **77/78** (2002) 437-443.
[13] K. Kadirvelu, P. Kanmani, P. Senthilkumar, V. Subburam, *Adsorp. Sci. Technol*. **22** (2004) 207-222.
[14] D. Mohan, V.K. Gupta, S.K. Srivastava, S. Chander, *Colloids Surf. A* **177** (2001) 169-181.
[15] G.G. Stavropoulos, P. Samaras, G.P. Sakellaropoulos, *J. Hazar. Mat.* **151** (2008) 414-421.
[16] K.P. Singh, A. Malik, S. Sinha, P. Ojha, *J. Hazard. Mat.* **150** (2008) 626-641.
[17] A.T.M. Din, B.H. Hameed, A.L. Ahmad, *J. Hazard. Mat.* **161(2-3)** (2008) *1522-1529*
[18] F. Villacanas, M.F.R. Pereira, J.M. Orfão, J.L. Figueiredo, *J. Coll. Int. Sci.* **293** (2006) 128-136.
[19] B.H. Hameed, A.A. Rahman, *J. Hazard. Mat.* **160(2-3)** (2008) *576-581*
[20] J.M. Valente Nabais, J.A. Gomes, Suhas, P.J.M. Carrott, C. Laginhas, S. Roman, J. Hazard. Mat., in press doi:10.1016/j.jhazmat.2009.01.075.