Metformin adsorption onto activated carbons prepared by hydrothermal carbonization and activation

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Introduction

The hydrothermal carbonization can be considered an environmental friendly process for the production of carbon materials with tailored properties, such as regular porous structure and specific surface chemistry. This process is easy to perform and uses mild temperatures without the use of solvents or gases, which results in a positive environmental balance when compared with the usual pyrolysis process [1]. Diabetes affects more than 152 million people in Europe and is on the rise all over the World. Metformin is one of the most used drugs to treat type 2 diabetes. This drug is an endocrine disruptor with a potential negative impact in the environment due to the fact that metformin is almost not metabolized in the human body and the incorrect disposal into the domestic garbage. Another relevant aspect is the danger of overdose intake of the drug that can lead to lactic acidosis, which in extreme cases can be lethal. The work now reported study the in vitro adsorption of metformin onto activated carbons using simulated gastric and intestinal fluids.

Materials and Methods

The precursor chitosan (Agros Organics) was submitted to a hydrothermal carbonization process using an autoclave heated in an oven at 200ºC for 24h using a water:precursor ratio of 1:6. The resulting char (Q200-24) was then activated in a horizontal furnace with carbon dioxide at 800ºC for 1, 3 and 5h (AC-1, AC-2, AC-3) and by chemical activation with $CaCO_3$ by impregnation with a ratio 1:10(w/v) followed by pyrolysis at 800ºC for 1, 3 and 5h (ACa-1, ACa-2, ACa-3). The sample AC-5 was oxidized with nitric acid at 900ºC for 1h (AC-5Ox). All materials were characterised by SEM, FTIR, elemental analysis and nitrogen adsorption isotherms at 77K. The metformin adsorption was done at 37ºC using gastric and intestinal simulated fluids with pH 1.2 and 7.5, respectively.

Results and Discussion

The results of the samples' characterisation can be seen in table 1. Regarding the elemental analysis we can see a notewhorthy nitrogen content, between 6 and 10%, which is attributed to the precusor used, naturally rich on nitrogen. The porous structure was well developed with apparent surface area (A_{BET}) within the range 420-1400m^2g^{-1} and pore volume and external area, as estimated by the alfa-S method (V_s and A_{ext}, respectively) in the range 0.18-0.69cm^3g^{-1} and 21-224m^2g^{-1}. All activated carbon samples have basic properties with point of zero charge (pzc) superior to 8. The

oxidation with nitric acid has lead to a decrease of the pzc value but without any significant change on the porous structure. By FTIR it was possible to identify the presence of several surface functional groups, namely hydroxyl, amines, carbonyl and lactones. The sample AC-5Ox shows the presence of carboxylic acid and ester.

Table 1. Characterisation of the samples

Sample	pH_{pzc}	Elemental analysis / %				Porous structure			
		C	N	H	O	A_{BET} /m^2g^{-1}	V_s /cm^3g^{-1}	A_{ext} /m^2g^{-1}	V_0 /cm^3g^{-1}
Chitosan	-	40.38	7.72	7.81	33.70	-	-	-	-
Q200-24	6.01	59.62	10.07	4.97	16.42	10	-	-	-
AC-1	9.34	75.94	5.80	1.23	8.73	423	0.18	24	0.17
AC-3	8.76	83.20	5.23	0.25	10.69	1095	0.44	21	0.42
AC-5	8.77	81.08	5.93	1.00	11.92	1023	0.41	18	0.39
ACa-1	-	80.06	5.92	0.87	9.13	642	0.29	19	0.28
ACa-3	-	81.13	5.25	1.04	10.47	852	0.36	22	0.34
ACa-5	-	85.32	5.45	0.93	12.85	1432	0.69	222	0.54
AC-5Ox	2.54	44.02	3.22	0.77	23.92	1034	0.46	36	0.38

The metformin maximum adsoprtion capacity in gastric (FG) and intestinal (FI) fluids is shown in table 2. We can see that adsorption is higher when FI is used. This difference cannot be only explained with the porous structure of the materials but also with chemical interactions between the nitrogen functional groups and metformin, reason why the adsorption onto sample Q200-24 is so high. The adorption mechanism seems to include also the electrostatic interactions that can explain the low adsortion in FG, where metformin is totally ionised aquiring a positive charge like the surface of the activated carbon samples.

Table 2. Metformin adsorption

Sample	FG/mgg^{-1}	FI/mgg^{-1}
Q200-24	-	32.0
AC-1	-	24.0
AC-3	1.5	28.0
AC-5	2.2	44.2
ACa-3	0.7	22.4
ACa-5	2.1	11.5
AC-5Ox	9.0	18.5

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References

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