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Activated carbon modification resulting in an enhanced Cr(VI) removal

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ABSTRACT

Two modification methods are used to enhance the adsorption properties of Cr(VI) of several activated carbons (AC). AC performance from brewer's spent grain (BSG) is compared with two commercials ACs: Norit GAC 1240 and Filtrasorb F400. The first modification consists of an oxidation of the surface using acidic and basic reagents. Elemental analysis reveals the oxidation of AC, but a removal of surface groups deteriorates adsorption properties. The second modification incorporates a copolymer with a quaternary ammonium end group on the surface of the AC. After copolymer modification a significant increase of nitrogen functionalities (+10%) is realised. An outspoken improvement (a factor of 5) in adsorption capacity and kinetics are proven to be solely caused by the copolymer. No synergic effect is found. Unmodified ACBSG is proven to exhibit the fastest adsorption kinetics for Cr(VI), but Cr_{tot} is removed fasted by copolymerised AC.

Keywords: Activated carbon; Adsorption; brewers' spent grain; Chromium; Copolymer modification

1. Introduction

Hexavalent chromium, Cr(VI), is present in all surface waters due to industrial and geological deposits [1,2]. In contrast to the essential Cr(III), Cr(VI) is carcinogenic and a toxic pollutant for both plants and living organisms [3–6]. The removal of Cr(VI) from aqueous solutions has been investigated using different adsorbents and composite materials [7–9]. The combination of adsorptive and reductive properties on biomass, bio-char, activated carbon (AC) or composite materials can remove Cr(VI) while also reducing it to Cr(III) [10–13].

To improve specific adsorption of Cr(VI), different modification techniques are investigated [14–17]. This work focuses on two types of modification in particular. The first modification is oxidation/acidification of the AC surface using nitric acid. Rivera-Utrilla et al. [14] concluded that treatment of AC with HNO_3 chemically enhanced the amount of surface oxygen functionalities such as carboxylic, phenolic and lactonic groups. This enhancement can lead to a better adsorption of metal ions, as a result of possible formation of complexes on the AC [18]. Especially for removal of chromium, Liu et al. [15] suggest a dual pathway process, where Cr(VI) is both adsorbed and reduced to Cr(III) by oxidation of the AC surface. The second modification technique involves the treatment of the AC with amine-crosslinked copolymers for improved chelation properties towards metal ions, Cr(VI) in particular [16]. In this approach, a nitrogen-rich copolymer is grafted on the available hydroxyl surface groups of the AC [17].

The goal of this work is to modify two commercial AC and AC derived from brewers' spent grain (BSG) for enhanced Cr(VI) adsorption and to test each of these for Cr(VI) adsorption. Worldwide BSG production is estimated at 30 Mt per year [19] and this waste is currently mostly fed to ruminants [20]. Possibilities for its use in different applications have

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been researched [19–29]. Production of in situ nitrogenised AC is proven to be an economically feasible process [30]. Two modifications are performed, acid treatment and grafting by a copolymer, to improve adsorption properties towards Cr(VI) and total Cr. Secondly, these ACs are characterised using complementary analytical techniques to monitor both modifications. Finally, a comparison between the adsorption isotherms and kinetics for Cr(VI) and total Cr is made.

2. Materials and methods

Milli-Q Millipore water (18.2 MΩ cm^{-1} conductivity) and analytical grade reagents are used in each experiment. Triethylamine, diethylenetriamine and epichlorohydrin are all ‘for synthesis’ grade. Norit GAC 1240 (Cabot Carbon) and Filtrasorb 400 (Calgon Carbon) are used to compare results of lab-scale AC with industrially available ACs.

2.1. Pyrolysis and activation

A two-step pyrolysis/activation reactor is used to prepare the AC from BSG, this setup is described by Vanreppelen et al. [30]. Oven-dried BSG is inserted in the reactor and pyrolysed from room temperature to 800°C with a continuous heating rate of 10°C min^{-1} in a nitrogen flow of 80 mL/min. An isothermal period at 800°C with water injection is used for activation. ACBSG02 is activated at 800°C for 30 min with 10 mL of water. ACBSG05 is also activated at 800°C but for a period of 45 min with 15 mL of water. These ACs were also produced for previous work [13,21,30].

2.2. AC modification

Two modifications are applied to ACBSG and to both commercially available ACs. The first modification is based on Liu et al. [15] and uses an acid/base (A/B) modification with HNO_3. Approximately 8 g of AC with 40 mL of 7 M HNO_3 solution is refluxed at 90°C for 15 h and subsequently dried at 105°C ± 5°C for 24 h. The dried AC is then added to 160 mL of an 1 M NaOH solution and shaken for 72 h at room temperature. The sample is washed until the effluent has a pH of approximately 7. Then it is dried again at 105°C ± 5°C for 24°h. The acid/base modified ACs are denoted with their name followed by the A/B notation.

The second modification consists of grafting an amino-crosslinked copolymer (CP) on AC [16,17]. In a typical preparation, 2°g of AC is introduced into a three-neck round bottomed flask, then stirred and heated to 80°C. Approximately, 5 mL of *N,N*-dimethylformamide (DMF) and 5 mL of epichlorohydrin are added. After 1 h, 3 mL of diethylenetriamine is added dropwise. Additionally, 10 mL of DMF is added to assure homogeneity of the mixture. After another 1 h, 5 mL of triethylamine is added. Finally, the sample is filtered after 1 h, washed with Milli-Q and dried in an oven at 70°C ± 5°C for 72 h. These ACs are denoted with their name followed by the CP notation. Apart from this standard preparation, different dilutions of reagent concentration (a half, a fifth and a tenth of the reagents) are applied to the best performing AC (ACBSG07) to achieve lower modification grades of the AC. The percentage of CP was calculated from the reagent amounts. The adsorption capacity of these ACs with different grades of CP-modification is compared to determine a possible synergic effect.

2.3. AC characterisation

Characterisation of non-modified ACBSGs has already been performed [13,30]. All modified ACs are analysed in a similar way as described by Bhatnagar et al. [18]. The AC and their modifications are sieved to particle size between 63 μm and 1 mm for characterisation and adsorption experiments.

Samples are mixed with liquid nitrogen and ground with mortar and pestle for Elemental Analysis (Thermo Finnigan Element Analysis Flash EA 1112). Calibration of the equipment is performed with BBOT (2,5-bis(5-tert-butyl-benzoxazol-2-yl) thiophene)). Samples are measured in quadruplicate. The ash content is calculated according to ASTM 2866-11, based on dry oxidation at 650°C ± 25°C for 3–6 h. Oxygen is calculated by difference.

To determine surface groups, a modified Boehm titration is performed as proposed by Velghe et al. [31]. In total, 200 mg of AC is made into contact with 25 mL of either a 0.100 M HCl or NaOH solution and shaken for 24 h in a thermostatic shaker. Titration is done by a Metrohm 794 Basic Titrino with 0.100 M NaOH or HCl, respectively, in a nitrogen atmosphere.

Scanning electron microscope (SEM) imaging is performed using a Hitachi TM3000 microscope for ACBSG02 and Norit GAC1240 and their modifications. The effect of AC type and modification is expected to be the same for ACBSG05 and Filtrasorb F400.

2.4. Adsorption isotherms and adsorption kinetics

Adsorption isotherm and kinetic experiments are performed using a solution of 10 mg/L Cr(VI) at pH 2. This solution is prepared using potassium dichromate and hydrochloric acid. The pH is chosen to promote Cr(VI) adsorption [32,33] and is monitored during the adsorption process by measuring after 4 and 20 h. Drifting pH was adjusted using an 1 M HCl solution.

Approximately, 5–100 mg of unmodified AC or modified AC is placed into closed vials and 25 mL of a 10 mg/L Cr(VI) solution is added and shaken for 24 h at room temperature. Based on the obtained adsorption isotherms of unmodified ACs, three additional experiments are performed by adding 10 mg of AC to 100, 200 and 500 mL of the same Cr(VI) solution. After shaking, the solution is filtered using ashless filters (A14, Carl Roth, Karlsruhe). The residual concentration of Cr(VI) is measured using the diphenylcarbazide method (DPC), measuring absorbance at 540 nm for both filtered and standard solutions [34]. Cr_{tot} is determined via inductively coupled plasma atomic emission spectroscopy (PE Optima 8300). This experiment is performed in duplo.

The adsorption capacity at equilibrium (q_e, in mg Cr/g AC) is calculated as follows:

$$q_e = \frac{\left(c_{\text{initial}} - c_{\text{equilibrium}}\right)\times V}{m_{\text{AC}}} \quad (1)$$

where c_{initial} (mg/L) is the concentration of the Cr solution added to the vial, $c_{\text{equilibrium}}$ (mg/L) the concentration of Cr after filtration, V the added volume (L) and m_{AC} (g) is the amount of AC added to the vial. These adsorption capacities are calculated for both Cr(VI) and Cr_{tot}. For Cr(VI) adsorption capacities, an apparent adsorption capacity is calculated in the same way to provide a q_{app}. This capacity is partially determined by adsorption and partially by reduction of the Cr(VI) to Cr(III). Removal percentage is calculated as follows:

$$\text{Removal percentage} = \frac{\left(c_{\text{initial}} - c_{\text{equilibrium}}\right)}{c_{\text{initial}}} \times 100\% \tag{2}$$

To determine whether the adsorbed amount (q_{app} in mg Cr(VI)/g AC or q_e in mg Cr_{tot}/g AC) is the result of a synergic effect between the copolymer and the AC, adsorption of Cr(VI) and total Cr are compared with unmodified AC adsorption results. ACs with different amounts of copolymer are added in two dosages: 25 mg of AC is added to 25 mL of a 10 mg/L Cr(VI) solution for an intermediate dosage setting (1 g AC/L), while 10 mg of AC is added to 200 mL of 10 mg/L Cr(VI) solution for a low dosage setting (50 mg AC/L).

Kinetic studies are performed for both the unmodified [13] and modified ACs. In total, 25 mL of a 10 mg/L Cr(VI) solution is added to 20 mg of AC in different vials and shaken during different time intervals. Samples are filtrated using ashless filters (Roth A14) and measured as described earlier. This test is performed in duplo.

Lagergrens pseudo-first-order (PFO) model [35,36] and the pseudo-second-order (PSO) model [37] are used to evaluate the results. The goodness of fit is evaluated using the correlation coefficient value (R^2). Both models are fitted using nonlinear regression. The PFO model can be expressed as follows:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{3}$$

q_t and q_e are the Cr adsorption capacities (in mg Cr/g AC) at time t and at time of equilibrium and k_1 (min^{-1}) is the PFO kinetic rate constant.

The PSO model can be expressed as follows:

$$q_t = \frac{k_2 q_e^{\,2} t}{1 + k_2 q_e t} \tag{4}$$

k_2 (min^{-1}) is the PSO kinetic rate constant.

3. Results and discussion

3.1. Characterisation of the ACs

Results from ash determination and elemental analysis are displayed in Table 1. A/B modification results in a lower carbon content due to oxidation of the surface. This is reflected in an increase in O/C atomic ratio. For Norit GAC 1240 and Filtrasorb 400, the O/C atomic ratio increases with a factor of 8 and 4, respectively. The ACs from BSG are less oxidised by the treatment, as they have higher initial oxygen content of approximately 10%. Their O/C ratio still increases with a factor of almost 2. The presence of oxygen-containing surface groups can promote the adsorption of Cr(VI) in two ways: preventing the reduction to Cr(III) and making more sites available for complexation [13,38].

The amino-crosslinked copolymer modifications (CP) drastically increase N, C and H concentrations, leading to lower oxygen percentage in the samples. The high nitrogen content in the copolymer itself leads to an increased N/C atomic ratio for all modified samples. There is also a sulphur impurity in one of the reagents, leading to approximately 0.5% sulphur present in all CP-modified samples.

Table 1
Ash content and elemental analysis of non-modified and modified ACs

Name	Ash (%)	C (%)	H (%)	N (%)	S (%)	O (%)** (by difference)	N/C atomic ratio	O/C atomic ratio
Norit GAC 1240 [13]	7.9 ± 0.1	85.3 ± 2.1	0.6 ± 0.1	0.8 ± 0.1	<DL*	5.4 ± 1.5	0.01	0.06
Norit GAC 1240 A/B	11.9 ± 0.3	58.1 ± 0.3	1.0 ± 0.1	0.7 ± 0.1	<DL	28.3 ± 0.4	0.01	0.49
Norit GAC 1240 CP	2.6 ± 0.1	68.4 ± 4.3	8.0 ± 1.2	12.1 ± 1.7	0.5 ± 0.1	8.4 ± 2.5	0.18	0.12
Filtrasorb 400 [13]	7.0 ± 0.1	83.7 ± 1.4	0.7 ± 0.1	0.9 ± 0.1	<DL	7.7 ± 0.4	0.01	0.09
Filtrasorb 400 A/B	9.4 ± 0.1	65.3 ± 0.5	1.6 ± 0.2	0.9 ± 0.1	<DL	22.7 ± 0.7	0.01	0.35
Filtrasorb 400 CP	2.2 ± 0.1	74.3 ± 2.3	6.0 ± 0.6	9.7 ± 0.6	0.5 ± 0.1	7.3 ± 3.0	0.13	0.10
ACBSG02 [30]	14.4 ± 0.5	71.0 ± 1.4	1.6 ± 0.1	2.7 ± 0.1	<DL	10.4 ± 1.5	0.04	0.15
ACBSG02 A/B	16.5 ± 0.1	60.8 ± 0.7	1.9 ± 0.1	3.2 ± 0.1	<DL	17.7 ± 0.8	0.05	0.29
ACBSG02 CP	4.5 ± 0.1	66.4 ± 0.3	8.1 ± 0.2	12.7 ± 0.6	0.5 ± 0.1	7.7 ± 0.9	0.19	0.12
ACBSG05 [30]	14.6 ± 0.3	70.5 ± 0.9	1.5 ± 0.1	2.5 ± 0.1	<DL	10.9 ± 0.9	0.04	0.15
ACBSG05 A/B	14.3 ± 0.1	62.5 ± 0.8	1.9 ± 0.1	3.3 ± 0.1	<DL	17.9 ± 1.0	0.05	0.29
ACBSG05 CP	4.8 ± 0.2	66.3 ± 0.8	7.7 ± 0.3	12.3 ± 0.4	0.5 ± 0.1	8.3 ± 0.3	0.19	0.13
Pure CP	<DL	50.7 ± 0.9	9.3 ± 0.2	15.3 ± 0.5	0.8 ± 0.2	23.9 ± 0.9	0.30	0.47

*, <DL: below detection limit; **, O calculated as 100% - Ash–C–H–N–S.

Table 2 shows the amount of acidic and basic surface groups in mmol/g on all ACs and their modifications. A/B modification drastically reduces all surface functionalities, acidic as well as basic. For example, Norit GAC 1240 leads to a reduction of acidic surface groups of 89% and a reduction of basic groups of 83%.

Table 2
Acidic and basic surface functionalities of non-modified and modified ACs

Name	Acidic surface groups (mmol/g)	Basic surface groups (mmol/g)
Norit GAC 1240 [13]	0.96	0.48
Norit GAC 1240 A/B	0.10	0.08
Norit GAC 1240 CP	0.11	0.21
Filtrasorb 400 [13]	0.58	0.47
Filtrasorb 400 A/B	0.12	0.06
Filtrasorb 400 CP	0.14	0.20
ACBSG02 [13]	0.70	0.65
ACBSG02 A/B	0.07	0.18
ACBSG02 CP	0.12	0.25
ACBSG05 [13]	0.78	0.80
ACBSG05 A/B	0.13	0.15
ACBSG05 CP	0.12	0.26
Pure CP	0.18	0.25

The incorporation of the copolymer changes the surface functionalities towards the properties of the copolymer itself. The properties of Filtrasorb 400 are less influenced by the copolymer, resulting in a slightly higher acidic group number and a lower amount of basic groups than the other copolymerised ACs. This is also confirmed by the lower N/C ratio for Filtrasorb 400.

The CP/AC ratio is determined gravimetrically and checked by calculation from the elemental analysis data. The AC-CP adsorbent contains approximately 66% CP.

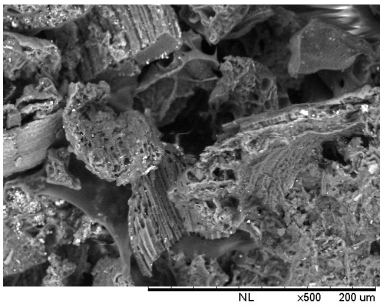
SEM images of ACBSG02 and Norit GAC1240 and their modifications are shown in Table 3. Comparing the two raw ACs, the difference between the coal-based Norit GAC1240 and the biomass-based ACBSG02 becomes clear. The structure of ACBSG02 is more unorganised and is similar to the structure of the biomass, whereas Norit GAC1240 has a smoother, organised surface. A/B modification does not alter the surface significantly. The PM modification leads to the formation of copolymer on the surface, completely blocking the original AC surface for both ACs.

3.2. Adsorption isotherms of Cr(VI) on modified ACs

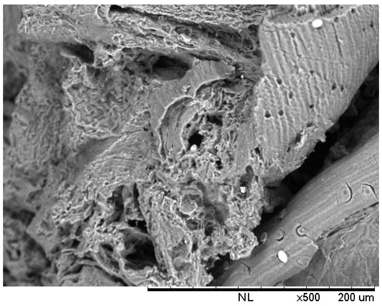
For clarity, only graphs of the ACBSG05 data are displayed. The data for ACBSG05, Norit GAC 1240 and Filtrasorb F400 all show the same trends.

Figs. 1 and 2 display the adsorption isotherms for Cr(VI) and Cr_{tot}, respectively, using ACBSG02 and its two modifications. Due to the reduction of Cr(VI) to Cr(III), the adsorption

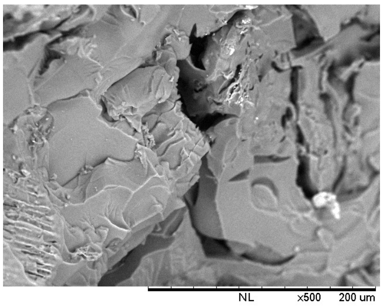
Table 3
SEM images of ACBSG02 and Norit GAC1240 and their modifications



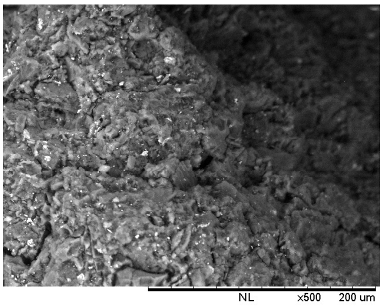
ACBSG02



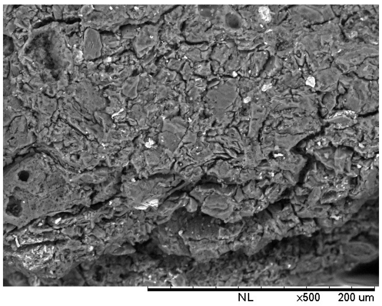
ACBSG02 A/B



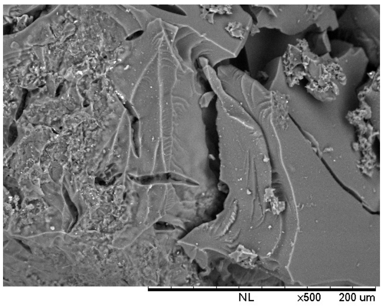
ACBSG02 PM



Norit GAC1240



Norit GAC1240 A/B



Norit GAC1240 PM

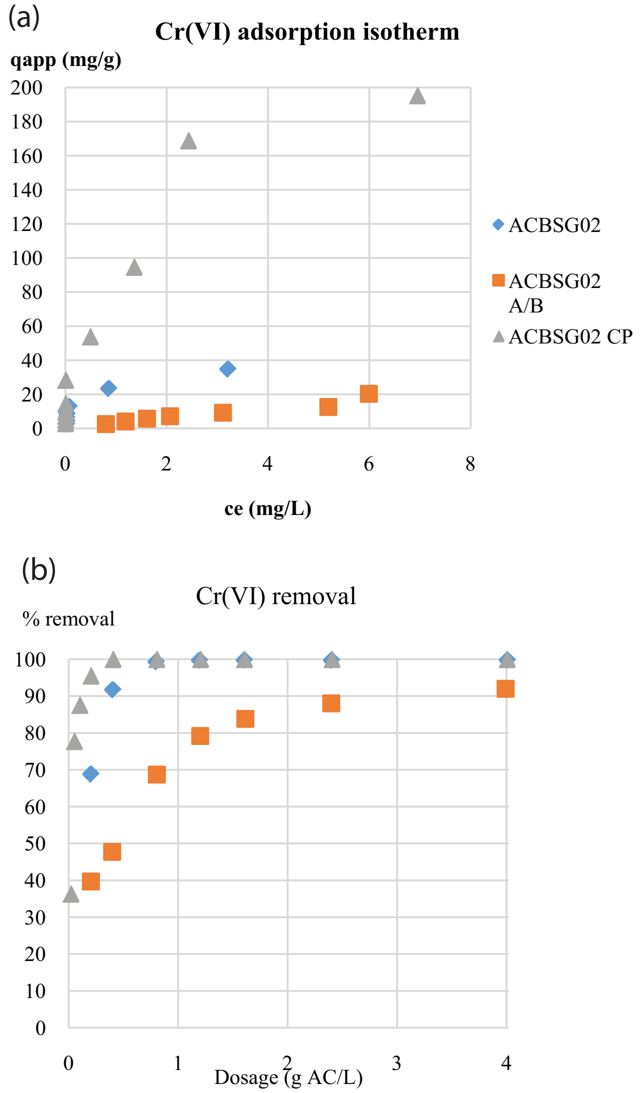


Fig. 1(a) Adsorption isotherm for Cr(VI) on unmodified and modified ACBSG02. (b) Removal percentage of Cr(VI) on unmodified and modified ACBSG02 as a function of AC dosage (5–100 mg of AC added to 25 mL of a 10 mg/L Cr(VI) solution at pH 2 and 10 mg of AC added to 100, 200, 500 mL of 10 mg/L Cr(VI) solution at pH 2).

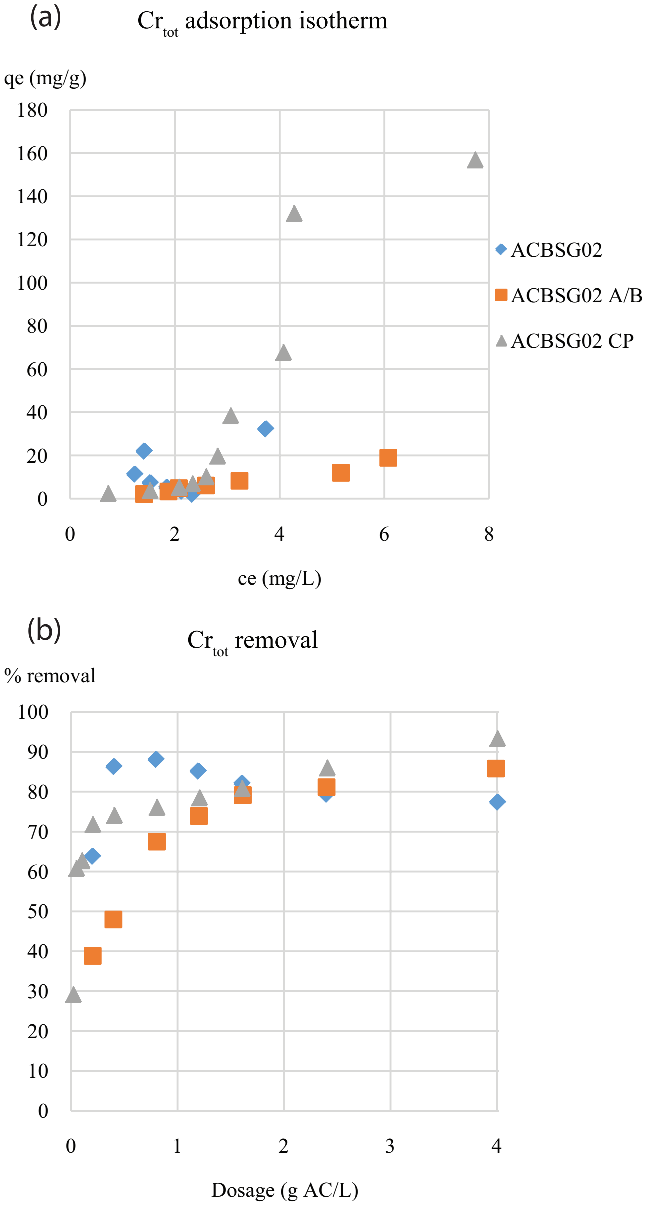


Fig. 2 (a) Adsorption isotherm for Cr$_{tot}$ on unmodified and modified ACBSG02. (b) Removal percentage of total Cr on unmodified and modified ACBSG02 as a function of AC dosage (5–100 mg of AC added to 25 mL and 10 mg of AC added to 100, 200, 500 mL of 10 mg/L Cr(VI) solution at pH 2).

capacity for Cr(VI) is only an apparent adsorption capacity [13]. Not all the Cr(VI) is adsorbed on the surface, a part of the Cr ions is still present in the solution as Cr(III). The AC treated with the CP modification reaches significantly higher q_{app} values for Cr(VI) as well as higher q_e values for Cr$_{tot}$ removal. Both A/B- and CP-modified ACs do not show an optimum AC dosage to combine adsorption and reduction as the unmodified AC does [13]. The Cr$_{tot}$ adsorption isotherm of the copolymer-modified AC shows an S-type isotherm, suggesting clustering of the Cr ions on the surface of the adsorbent. For adsorption on the A/B-modified AC, both isotherms seem to be of the L-type, but very low values of q_e are reached, making this the least effective adsorbent, especially at low dosage. Even though a higher concentration of oxygen in the AC is expected to improve Cr(VI) adsorption, the removal of surface functionalities seems to limit adsorption severely. For ACBSG07, Norit GAC1240 and Filtrasorb and their modifications, the same conclusion can be formulated.

Table 4 summarises values for adsorption capacities q_e from the adsorption studies and for comparison with literature values for adsorption of Cr(VI). Different types of adsorbents and details of experimental parameters are displayed, such as measurement method and concentration ranges. The most important parameters that influence the found q_{app} and q_e are adsorbent dosage and Cr(VI) concentration. The pollutant/adsorbent ratio increases when using low doses of AC or high Cr(VI) concentrations, resulting in an increased

Table 4
Adsorption capacities for Cr(VI) found in literature and in the present study

Adsorbent	Temperature (°C)	Measurement method	Adsorption capacity q_e (mg/g)	Optimal pH	Dosage (g AC/L)	Concentration of Cr(VI) (mg/L)	References
Arundo donax Linn AC	NS[a]	DPC/AAS	90.99	5	1	10–100	[16]
Arundo donax Linn AC - EDT	NS	DPC/AAS	102.88	5	1	10–100	[16]
Groundnut husk AC	30	AAS	7.01	3	0.625-7.5	10	[11]
Groundnut husk AC silver impregnated	30	AAS	11.4	3	0.625-7.5	10	[11]
$CoFe_2O_4$/activated carbon composite	NS	DPC	32.4	2	4	50–150	[9]
Carya peels based activated carbon (Changnan Activated Carbon Co.)	NS	DPC	33.8	2	4	50–150	[9]
Norit GAC1240	25	DPC/ICP OES	84/60[b]	2	0.2–4	10	Present study
Norit GAC1240 A/B	25	DPC/ICP OES	33/31[b]	2	0.2–4	10	
Norit GAC1240 CP	25	DPC/ICP OES	181/156[b]	2	0.2–4	10	
Filtrasorb F400	25	DPC/ICP OES	76/58[b]	2	0.2–4	10	
Filtrasorb F400 A/B	25	DPC/ICP OES	30/30[b]	2	0.2–4	10	
Filtrasorb F400 CP	25	DPC/ICP OES	178/135[b]	2	0.2–4	10	
ACBSG02	25	DPC/ICP OES	20/13[b]	2	0.2–4	10	
ACBSG02 A/B	25	DPC/ICP OES	16/14[b]	2	0.2–4	10	
ACBSG02 CP	25	DPC/ICP OES	195/157[b]	2	0.2–4	10	
ACBSG05	25	DPC/ICP OES	35/30[b]	2	0.2–4	10	
ACBSG05 A/B	25	DPC/ICP OES	19/16[b]	2	0.2–4	10	
ACBSG05 CP	25	DPC/ICP OES	207/169[b]	2	0.2–4	10	

[a] NS, not specified

[b] q_e for Cr(VI)/total chromium.

q_{app}/q_e value. In most research, only Cr(VI) concentrations are measured by the DPC method. Some authors mention the monitoring of both Cr(VI) and Cr_{tot}, but do not report separate q_e values. Reduction of Cr(VI) also plays a role in adsorption performance on AC and therefore measurement of both Cr(VI) and Cr_{tot} is necessary. Comparing solely the q_e values, ACBSG performs averagely compared with other ACs from biomass as listed in Table 4 (keeping in account their higher starting concentrations).

3.3. Influence of AC/CP ratio on adsorption capacity

In Figs. 3 and 4, the q_e values for Cr(VI) and total Cr adsorption are displayed for different ratios of copolymer to AC. On the left hand, the results indicate q_e values for pure AC (0% copolymer), the result to the right is compared with pure copolymer (100%). At both low (0.05 g/L) and intermediate (0.8 g/L) dosage of AC, there is a decrease in efficiency of the adsorbent grafted with 6% to 11% of copolymer. This result suggests that the copolymer does not increase the efficiency of the AC, but the copolymer itself is important for the improved adsorption at higher levels. Furthermore, the copolymer blocks the porous structure of the AC. There is not enough copolymer to increase the adsorption efficiency in order to compensate for this effect. At copolymer concentrations above 30%, the AC only works as a carrier material and does not significantly contribute to the adsorption and only reflects the adsorption potential of the copolymer. In contrast, only at higher levels of copolymer (>30%) and at intermediate AC dosages, q_e values are comparable with pure AC reflecting no real added adsorption value of the copolymer.

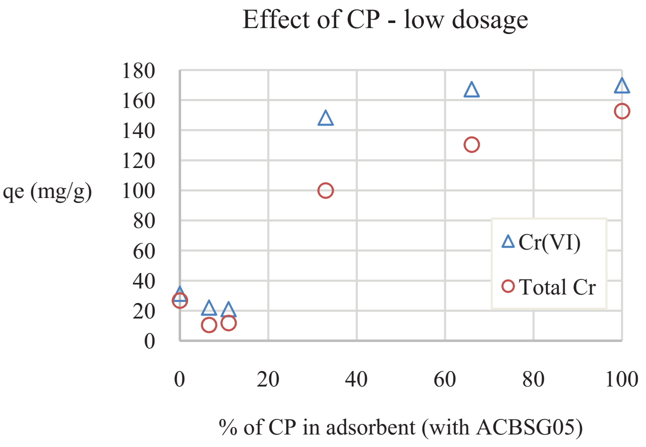


Fig. 3. Adsorption capacity of ACBSG05 CP with different levels of copolymer at low dosage (0.05 g AC/L, 10 mg AC + 200 mL of 10 mg/L Cr(VI) solution at pH 2).

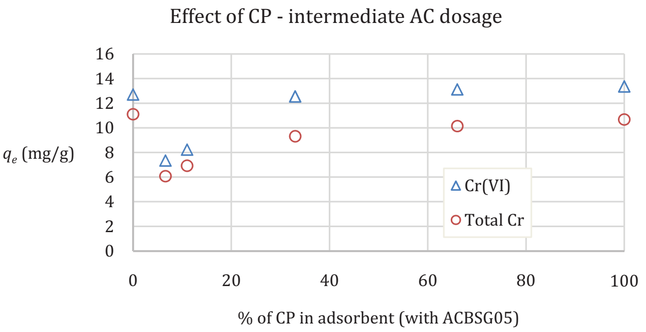


Fig. 4. Adsorption capacity of ACBSG05 CP with different levels of copolymer at intermediate dosage (1 g AC/L, 25 mg AC + 25 mL of 10 mg/L Cr(VI) solution at pH 2).

3.4. Adsorption kinetics

Figs. 5 and 6 show the kinetic adsorption data of ACBSG05 and its A/B and CP modifications for Cr(VI) and Cr_{tot}. Plotted lines represent the PSO model.

The other ACs (ACBSG05, Norit GAC 1240 and Filtrasorb 400, and their A/B and CP modifications) showed the same graphical trends. All ACs reach equilibrium after 16 h.

PFO and PSO reaction rates are determined for ACBSGs as well as for the commercially available ACs, both for Cr(VI) and Cr_{tot}. The reaction kinetics are slightly better fitted by the PSO model, displaying the results in Table 5 for all kinetic experiments.

The kinetic constant for the PSO model shows that unmodified ACBSG adsorbs Cr(VI) faster than any other AC (kinetic constant k_2 = 0.091 min^{-1} and k_2 = 0.107 min^{-1} for

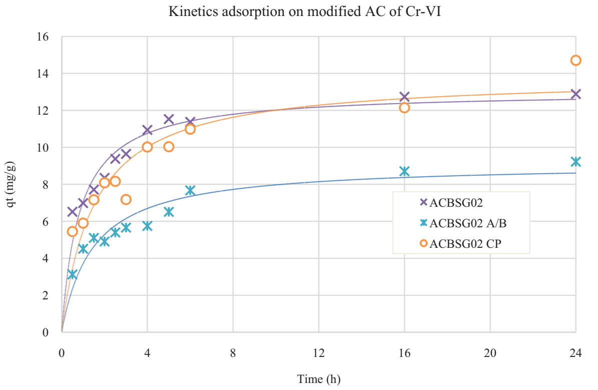


Fig. 5. Kinetics of the adsorption of Cr(VI) on unmodified and modified ACBSG02 (20 mg AC + 25 mL 10 mg/L Cr(VI) solution at pH 2).

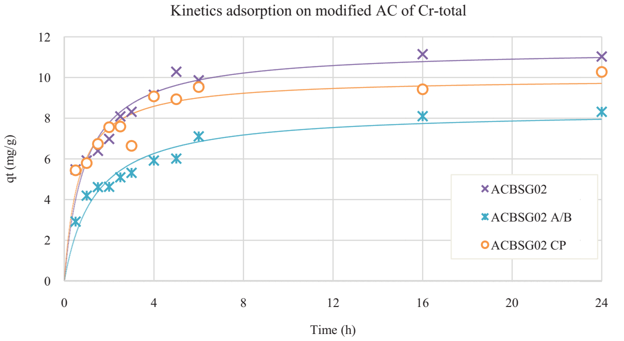


Fig. 6. Kinetics of the adsorption of Cr_{tot} on unmodified and modified ACBSG02 (20 mg AC + 25 mL 10 mg/L Cr(VI) solution at pH 2).

Table 5
Calculated kinetic constants according to PSO and PFO models for each AC and their modifications, for both Cr(VI) and Cr_{tot}

Sample name	Cr(VI)						Cr_{tot}					
	PFO			PSO			PFO			PSO		
	k_1 (min^{-1})	q_{max} (mg/g)	R^2	k_2 (min^{-1})	q_{max} (mg/g)	R^2	k_1 (min^{-1})	q_{max} (mg/g)	R^2	k_2 (min^{-1})	q_{max} (mg/g)	R^2
Norit GAC1240	0.47	12.08	0.904	0.047	13.55	0.934	0.52	9.16	0.899	0.072	10.21	0.920
Norit GAC1240 A/B	0.29	11.70	0.955	0.026	13.52	0.977	0.30	10.41	0.958	0.030	11.99	0.977
Norit GAC1240 CP	0.52	11.70	0.934	0.054	13.12	0.980	0.82	9.18	0.950	0.124	9.18	0.970
Filtrasorb F400	0.50	12.31	0.940	0.049	13.84	0.953	0.55	9.78	0.926	0.071	10.92	0.924
Filtrasorb F400 A/B	0.24	11.46	0.979	0.019	13.63	0.980	0.27	10.41	0.956	0.026	12.09	0.960
Filtrasorb F400 CP	0.53	11.73	0.854	0.056	13.16	0.938	0.78	9.14	0.863	0.114	10.13	0.952
ACBSG02	0.77	11.82	0.823	0.091	13.04	0.915	0.70	10.36	0.842	0.094	11.41	0.909
ABSG02 A/B	0.49	8.21	0.811	0.075	9.14	0.898	0.52	7.50	0.847	0.087	8.40	0.930
ACBSG02 CP	0.47	12.35	0.787	0.047	13.84	0.863	0.99	9.06	0.691	0.155	9.97	0.828
ACBSG05	0.92	11.87	0.838	0.107	13.10	0.838	0.88	10.26	0.836	0.118	11.33	0.911
ACBSG05 A/B	0.44	9.51	0.910	0.054	10.75	0.963	0.49	8.66	0.900	0.067	9.76	0.962
ACBSG05 CP	0.56	11.70	0.869	0.060	13.07	0.937	1.05	9.17	0.759	0.168	10.03	0.896

ACBSG02 and ACBSG05, respectively). This higher kinetic rate might be due to the combination of adsorption and reduction of Cr(VI).

For total Cr, the kinetic constant is the highest for the copolymerised ACs, suggesting a rapid uptake of all Cr ions. The copolymerised ACBSGs have a somewhat smaller particle size distribution, resulting in a higher k_2 value. The oxidised ACs are slower than the unmodified ACs because of reduced interaction sites as a result of lower amounts of surface groups.

4. Conclusion

A first modification of AC by acidic/basic treatment does not improve the surface characteristics of any of the produced ACs from BSG. Even though the oxygen content increases, the amount of surface groups is more critical for the adsorption of Cr(VI). The adsorption capacity q_e decreases by this modification method. Incorporation of a copolymer with quaternary ammonium end groups on the surface of the AC greatly enhances the adsorption, especially at low dosage, but the effect is solely caused by the copolymer. There is no synergy between the copolymers and the surface of the AC. The AC only served as a bulk carrier for the copolymer and its chemical and physical properties were of minor importance. In an industrial setting, other carrier materials are probably better economically suited for this purpose. Kinetic experiments also show that ACBSGs have a faster removal rate for Cr(VI) than the two commercially available ACs and their modified versions. The removal of Cr_{tot} was fastest on all copolymerised ACs, where smaller particle size promotes adsorption kinetics.

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