# Modification of activated carbons from brewers' spent for chromium(VI) adsorption

## Introduction

Brewers' spent grain (BSG) accounts for 85% of brewery waste [1, 2], with an average production of 14-20 kg per 100 L of beer [3]. The total production of beer in Europe (EU-27, for 2011) amounts up to 38400 ML/year, producing up to 5.38 – 7.68 Mt of wet BSG to be disposed of every year [4]. Worldwide production of BSG is estimated at 30 Mt per year [5]. Using pyrolysis followed by steam activation, BSG can be converted into activated carbon (AC) with high nitrogen content for the purification of liquid or gaseous waste streams [6]. Nitrogenised AC has already shown excellent adsorption properties for different pollutants [7-12]. This enhanced adsorption is a result of the overall change in acidic/basic functionalities of the AC [13] and a possible combination of physisorption and chemisorption [8].

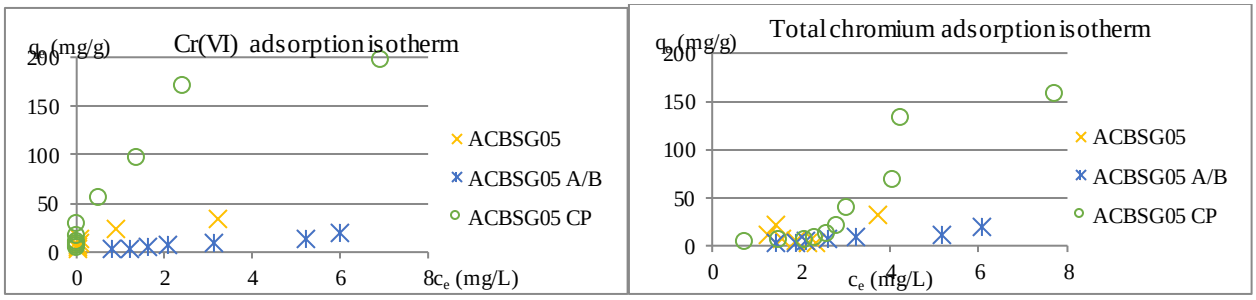
To improve specific adsorption of Cr(VI), different modification techniques have been investigated. This work focuses on two types of modification in particular. The first modification is oxidation/acidification of the AC surface using nitric acid. Rivera-Utrilla et al. [14] concluded that treatment of AC with $HNO_3$ chemically enhanced the amount of surface oxygen functionalities such as carboxylic, phenolic and lactonic groups. This enhancement leads to a better adsorption of metal ions, owing to possible formation of complexes on the AC [15]. Liu et al. [16] 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 is to modify the AC with amine-crosslinked copolymers for improved chelation possibilities towards metal ions, Cr(VI) in particular [17]. This technique grafts a nitrogen-rich copolymer on the available hydroxyl surface groups of the AC [18].

## Materials and methods

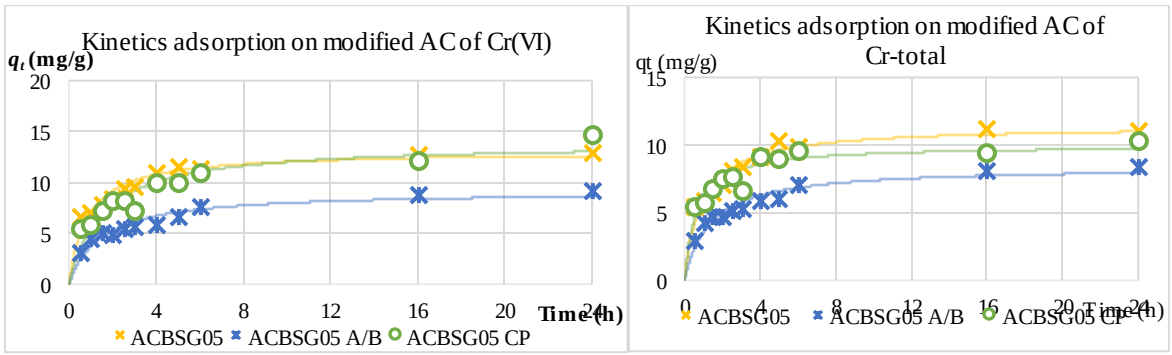
Preparation of the AC was conducted in a horizontal semi-continuous reactor as described in [21]. Two modifications were applied to ACBSG and to both commercially available ACs. The first modification was based on Liu et al. [33] and used an acid/base (A/B) modification with $HNO_3$. The second modification technique is to modify the AC with amine-crosslinked copolymers for improved chelation possibilities towards metal ions, Cr(VI) in particular [34]. This technique grafts a nitrogen-rich copolymer (CP) on the available hydroxyl surface groups of the AC [35].

For the determination of adsorption isotherms and kinetics a solution of 10 ppm Cr(VI) at pH 2 was prepared using potassium dichromate and hydrochloric acid. It was proved that a low pH promotes Cr(VI) adsorption [38, 39] (see also Table 3.) For determination of the isotherms, masses of AC between 5 and 100 mg were placed into closed vials together with 25 mL of the Cr(VI) solution and shaken for 24 h. The pH was adjusted back to 2 after 4 and 20 h. After shaking, the solution was filtered using ashless filters and Cr concentrations were determined. The concentration of Cr(VI) was measured using the diphenylcarbazide method [40]. Total Cr was determined via ICP-AES. An investigation of kinetics was done by bringing 20 mg of AC into contact with 25 mL of 10 ppm Cr(VI) solution in different vials and measuring total Cr and Cr(VI) concentrations after filtration with ashless filters at several time intervals. Evaluation of the Cr(VI) and total Cr adsorption kinetics were performed using both Lagergrens pseudo first order model [41, 42] and the pseudo second order (PSO) model as proposed by Ho and McKay [43].

## Results




As can be seen from the figures, the AC treated with the CP modification reached significantly higher $q_e$ values for Cr(VI) as well as for total Cr removal. Adsorption isotherms for Cr(VI) show a decreasing $c_e$ with increasing AC dosage as L-type isotherms. The total Cr adsorption isotherm on 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. For ACBSG07, Norit GAC1240 and Filtrasorb and their modifications the same conclusion can be formulated.




The kinetic constant for the PSO model showed that unmodified ACBSG adsorbs Cr(VI) faster than any other AC (kinetic constant $k_2 = 0.091$ and $k_2 = 0.107$ for ACBSG05 and ACBSG07 respectively). This higher kinetic rate might be due to the combination of adsorption and reduction of the Cr(VI). For total Cr, the kinetic constant was the highest for the copolymerised ACs, suggesting a rapid uptake of all Cr ions. The oxidised ACs were much slower than the unmodified ACs because of reduced interaction sites as a result of lower amounts of surface groups.

## Conclusion

AC from BSG is a viable adsorbent for removal of chromium from waste water streams at the tested concentration of 10 mg/l Cr at pH 2, with an optimal dosage of 0.75 g/L. The modification of the AC by acidic/basic treatment does not improve the surface characteristics of the ACs, nor does it improve the adsorption capacity $q_e$. Incorporation of a copolymer with a quaternary ammonium end group on the surface of the AC greatly enhances adsorption, 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. AC from BSG is best used for chromium removal in its pure form, as the removal percentages at intermediate (optimal) dosages are similar to the copolymerised AC.

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