CHEMICAL ENGINEERING TRANSACTIONS
VOL. 105, 2023
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: David Bogle, Flavio Manenti, Piero Salatino

ISBN 979-12-81206-04-5; **ISSN** 2283-9216
DOI: 10.3303/CET23105060

Evaluation of Activated Carbon Treatment in the Decolourization of Starch Hydrolysates

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Starch hydrolysates, typically produced by enzymatic hydrolysis of starch from different raw materials, are presented as glucose syrups with a brownish colour due to colour compounds formed during the processing. The colour must be removed for further commercial use, usually done by activated carbon (AC) downstream treatment. This research studied the decolourization of starch hydrolysates with AC to evaluate better optimum process conditions, thus help reducing resource consumption and waste generation in the actual downstream systems. Adsorption by powdered NORIT GBSP AC was carried out in a lab-scale batch process at a constant temperature (70 °C) for different contact times in a range of 5 to 90 minutes, AC dosages from 0.1 to 0.8 g / 100 ml solution and sugar concentrations of 16, 20, 30, and 40 Brix. The results showed that the adsorption time to reach equilibrium decreases with higher dilution (10, 20, 30 and 60 min for 16, 20, 30 and 40 Brix solution). All dilutions achieved decolourization from 85 % to 90 %, with colour reduced to nearly 50 ICUMSA Units. Regarding the obtained product sugar, a lower amount of AC is required for higher sugar concentration (0.020, 0.021, 0.021, and 0.010 g AC per g decolourised sugar for 16, 20, 30, and 40 Brix). For better determination of best decolourization conditions, further investigation of the correlation between faster adsorption with higher water and energy consumption and lower dilution for less required AC is required. Additional studies in other separation techniques are proposed, especially membranes, showing high AC waste reduction potential.

1. Introduction

Starch, primarily used for food products, is present in most plant tissues but is mainly obtained from maize, wheat, potatoes, and tapioca (cassava, manioc) (Peter, 2010). In the EU and UK, most starch is used for saccharification products, such as glucose syrups accounting for 49 % in 2021 (VGMS e.V.,2021). Glucose syrups are the hydrolysis products of starch consisting of some glucose monomer, varying quantities of dimer, oligosaccharides, and polysaccharides, and many other carbohydrates as by-products dependent on the syrup in question and its process of manufacture (Kearsley & Dziedzic, 1995). Depending on the product's dextrose equivalent (DE), it has a broad spectrum of applications (Clark et al., 2014).
The depolymerisation of starch, called thinning, liquefaction, or conversion, can be achieved by applying acid, heat and/or enzymes to cooked starch (Höfer, 2015). The hydrolysis process can be carried out either by acid, enzyme, or a combination of both (Clark et al., 2014). During the processing, browning in the syrup occurs due to the Maillard Reaction because of some reducing sugars react with amino groups content, as well as due to caramelisation during high temperatures at manufacturing (Peter, 2010). The colour can usually be removed by applying adsorption with activated carbon (AC) (Peter, 2010).
Detailed studies were conducted on the adsorption process parameters and mechanism for AC on date syrup (Nasehi et al., 2012) and ion exchange resin on Maillard reaction products (Serpen et al., 2007). A study on glucose syrup was carried out by (Çelebi & Kincal, 2007), investigating the effect of different AC and manufacturing conditions on decolourization. For a more efficient manufacturing of high-quality glucose syrup, an investigation of the understanding of various process parameters at decolourization by AC is required,

Paper Received: 28 January 2023; Revised: 12 May 2023; Accepted: 21 September 2023
Please cite this article as: Trischack A., Cabeza C.A., Ahmed A.E.G., Minauf M., Harasek M., 2023, Evaluation of Activated Carbon Treatment in the Decolourization of Starch Hydrolysates, Chemical Engineering Transactions, 105, 355-360 DOI:10.3303/CET23105060

especially the correlation between sugar and colour concentration, AC dosage and adsorption time. Thus, this study aims to investigate the effect of the change of several process conditions on the decolourization treatment by AC for better management of resources and solid waste generation.

2. Materials and Methods

2.1 Syrup

Organic glucose syrup from maize starch hydrolysates provided by AGRANA Stärke GmbH, which had been concentrated to approximately 70 Brix for storage. For experiments, the syrup was diluted with deionised water at room temperature until a desired homogeneous sugar concentration of 16, 20, 30 and 40 Brix. The pH of the diluted solutions was between 4.7 and 4.9. During the study, two batches with similar characteristics were used, referred to as 1st and 2nd batches. The 1st batch was used for 30 Brix dilutions at equilibrium and kinetic experiments with 0.6 g/100 AC dosage; all other experiments were carried out with the 2nd batch.

2.2 Activated Carbon

Powdered activated carbon (AC) (Norit GBSP) was used as an adsorbent in this study to decolourise the syrup, which is highly suitable for applications in the food industry, especially in the purification of certain starch hydrolysates. The AC was weighted in dosages of 0.1, 0.15, 0.2, 0.3, 0.4, 0.6, and 0.8 g per 100 ml solution with an accuracy of two digits.

2.3 Experimental Setup

The adsorption process was done in a batch lab-scale experiment in a shaker with a heated water bath (70 °C) with 100 ml Erlenmeyer flasks. The flasks were filled with a certain AC dosage, and adsorption started by adding 50 ml of the diluted syrup and placing it into the shaker. Flasks were covered with aluminium foil to prevent contamination by evaporating water from the water bath. Adsorption time was 40 minutes for equilibrium experiments. Kinetic experiments were carried out with 5, 10, 20, 30, 40, 60, and 90 minutes with all dilutions and different AC dosages of 0.1, 0.3, 0.6 and 0.8 g AC / 100 ml with a dilution to 30 Brix.
Separation of AC from the treated solution was carried out by vacuum filtration with a Buchner funnel and filter paper sartorius stedim grade 391 (particle retention 2-3 µm). The filtration started immediately after the sample was taken from the shaker. The funnel and the flask were cleaned with deionized water afterwards.

2.4 Analytic Methods

Conductivity and pH were measured with VWR MU 6100 H multiparameter. Sugar content was analysed by determining Brix in g saccharose per g solution with an Optronic Digital Refractometer from KRÜSS DR6200-T at 20 °C. Decolourization was investigated by absorption measurement with the UV-vis spectrometer UV 1800 from Shimadzu at a wavelength of 420 nm.
Colour is calculated according to the ICUMSA method (Whalley, 1964) with the light absorbance of the solution at a wavelength of 420 nm with distilled water as a reference. The colour in IU (ICUMSA Units) can be calculated by the absorbance or transmittance colour with the following equation.

$$Colour = \frac{1000 \cdot A}{b \cdot c} \tag{1}$$

With the absorbance A at 420 nm, the length of the absorbing path b, which is 1 cm and the concentration c of total solid concentration in g sugar per ml. Relative removal of colour and sugar is determined by

$$Colour/Sugar\ reduction = \left(1 - \frac{Colour/Sugar\ after}{Colour/Sugar\ before}\right) \cdot 100\%. \tag{2}$$

For statistical verification, all experiments are carried out in triplicates. For the determination of equilibrium time and optimum dosage, analysis of variance (ANOVA) with a significance level of 5 % is used. Nonlinear regression is done to investigate the best several adsorption isotherm models.

2.5 Adsorption Isotherms

Adsorption isotherms describe the relationship between the adsorbate concentration on the solid and the respective equilibrium concentration in the bulk fluid phase at a constant temperature. (Gawande et al., 2017) The mathematical correlation usually is graphically expressed by the adsorbed concentration q_e against its residual concentration in the fluid C_e (Foo & Hameed, 2010), which is achieved by experiments and then correlated to other isotherm models for further design and modelling (Ramaswamy et al., 2013).

Langmuir Isotherm

The Langmuir isotherm (Langmuir, 1932) is one of the first explanations of the adsorption phenomena. Langmuir explained adsorption based on kinetic arguments, where molecules strike onto the surface continually with corresponding evaporation (desorption) of molecules from the surface at the same rate at equilibrium (Do, 2008). The following assumptions are used: Homogeneous surface with constant adsorption energy over all sites, adsorption is localized, and each site can accommodate only one molecule or atom (Do, 2008). With the constant K_L and the maximum load of the adsorbent q_{max}, the Langmuir equation for solutions is defined as:

$$q_e = q_{max} \frac{K_L \cdot C_e}{1 + K_L C_e} \tag{3}$$

Freundlich Isotherm

The Freundlich isotherm describes multilayer adsorption, where the bond strength in positions close to the surface is stronger and decreases with the increasing filling rate of the positions (Ghaedi, 2021). It is widely used to analyse the adsorption of aqueous solutions (Worch, 2021), especially the adsorption of organics from aqueous systems on activated carbon (Do, 2008). This model does not determine the maximum adsorbing capacity and cannot describe the linear behaviour at very low concentrations, which is why it is best applicable at medium-range adsorbate concentrations (Ghaedi, 2021; Worch, 2021). With the adsorption coefficient K_f and Freundlich exponent the n_f the Freundlich equation is defined as:

$$q_e = K_f \cdot C_e^{n_f} \tag{4}$$

3. Results and Discussion

3.1 Kinetics

Results in Figure 1 (a) show slightly similar capabilities of colour removal for all dilutions but 30 Brix. Worse capability in 30 Brix possibly is explained due to the use of a different batch, the 1st batch, which generally showed worse decolourization behaviour in the experiments. Statistical analysis of maximum colour removal proved no differences for dilutions of 16, 20 and 40 Brix, thus dilution does not affect maximum decolourization capacity. For optimum decolourization, it is of the main interest that AC adsorbs as much as possible, which is achieved after equilibrium time. With increasing dilution, the equilibrium time decreases, see Table 1. Thus, it can be concluded that higher dilutions are more efficient in terms of less required decolourization time.
From the results of experiments with different AC dosages, it can be concluded that decreasing dosage leads to less adsorption capability and requires longer contact time to reach equilibrium, see Figure 1 (b) and Table 1.In relation to different dilutions and AC dosages, it can be concluded, that the highest efficiency will be achieved with high dilution and dosage. However, both parameters will reach a maximum in decrease of contact time, and AC dosage will have a maximum in colour removal. On the other hand, with an increase in dilution, more water is required, which leads to higher energy needed for heating the solution in the process and in the concentration by evaporation of the added water storage purposes. Thus, finding an optimum between these factors is necessary.

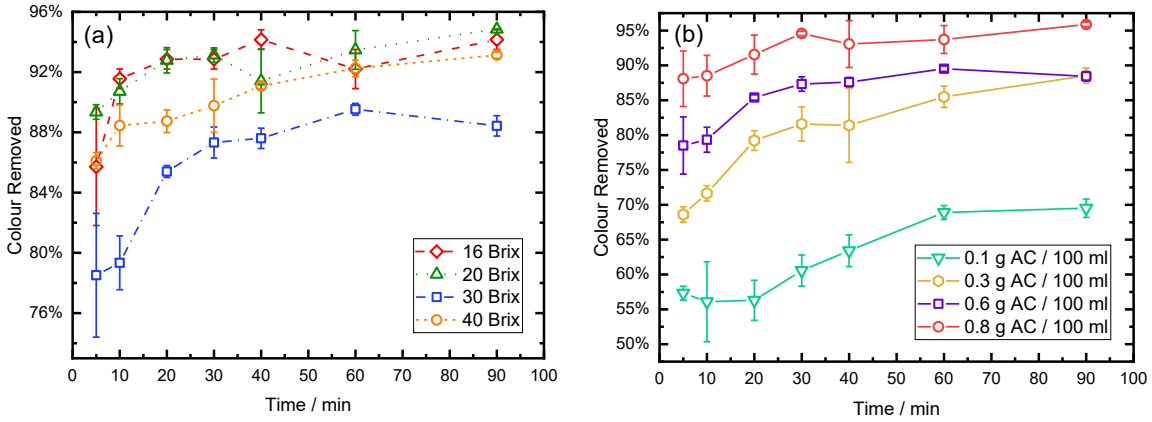

Figure 1: Decolourization over time with different sugar content for AC dosages of 0.6 g / 100 ml in (a) and different AC dosages with dilutions to 30 Brix in (b)

Table 1: Equilibrium time for several dilutions and AC dosages

Dilution	Equilibrium time / min	Colour removed at equilibrium
16 Brix	10	92 %
20 Brix	20	93 %
30 Brix	30	87 %
40 Brix	60	92 %

AC dosage / g/100ml	Equilibrium time / min	Colour removed at equilibrium
0.1	60	69 %
0.3	30	82 %
0.6	30	87 %
0.8	5	94 %

3.2 Decolourization

Obtained curves for decolourization with different AC dosages show only a slight difference between different dilutions, as presented in Figure 2. Optimum dosages for maximum decolourization, see Table 2 decreases slightly with the dilution and so content of colour molecules. It should be mentioned that the experiment with a dilution of 30 Brix was carried out with the 1st batch, which leads to small differences in the results. Overall, the AC was able to remove most colour in all dilutions, with removal from 85 to 90 % and no significant difference was obtained between the different dilutions. Since carbohydrates are the main product, knowing the required relative AC dosage per gram of obtained sugar is mandatory. Results of the relative AC dosage in Table 2 show same required dosages for dilutions from 16 to 30 Brix, while 40 Brix required only half the amount of AC for the same amount of obtained sugar. Since the 1st batch used for the 30 Brix dilution showed in generally bit less decolourization behaviour, it can be assumed that with a higher concentration of sugar and thus colour the required AC will be decreased. In contrast to the conclusion of kinetic experiments, the best conditions for efficiency improvement by reduction of AC amount would be a low dilution of the syrup. However, lower dilution leads to higher viscosity, which would worsen the filtration of AC. This was the case in the experiment with 40 Brix, where filtration time was increased significantly. On the other hand, high viscosity aggravates intraparticular diffusion, and higher sugar concentration will at one point worsen the decolourization behaviour. Therefore, the reduction of AC with higher sugar concentration is limited.

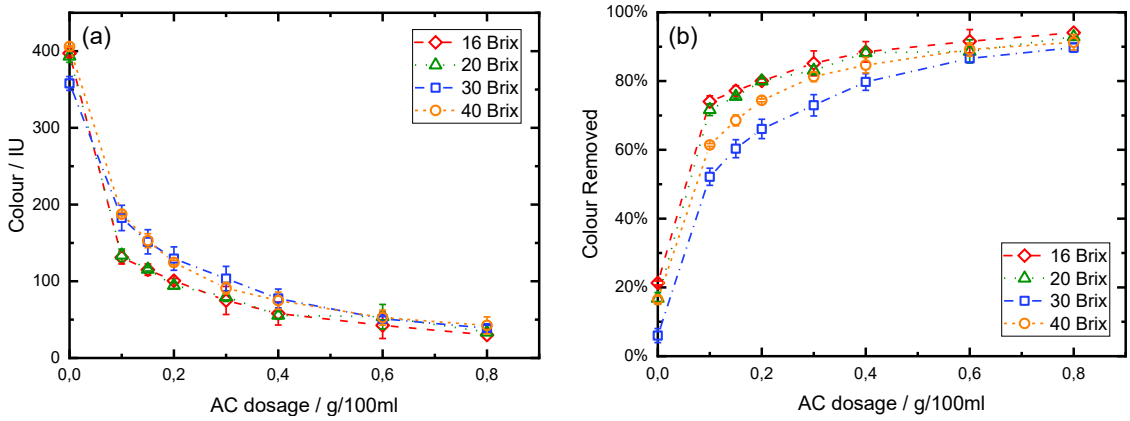

Figure 2: (a) Colour values and (b) colour removed percentages after decolourization with AC

Table 2: Optimum AC dosages for decolourization and colour removed.

Dilution	Optimum Dosage / g/100ml	Saccharose content after adsorption / g	Required g AC per g Saccharose	Colour removed at optimum dosage	Remaining colour at optimum dosage / IU
16 Brix	0.3	7.54	0.020	85 %	75
20 Brix	0.4	9.37	0.021	88 %	56
30 Brix	0.6	14.39	0.021	87 %	51
40 Brix	0.4	20.03	0.010	85 %	75

The colour removal due to AC separation was analysed by investigation of the decolourization experiment without AC with and without following filtration. Results in Figure 3 show that colour can be reduced by the filter paper by approx. 100 IU respectively 20 %. This means more than 20 % of colour molecules need to have a size greater than 2-3 µm. Thus, pre-treatment with filtration could be a proposed process method for the reduction of required AC, as already shown by (Cabeza et al., 2022) with 27 % colour removal of starch hydrolysates by ultrafiltration and by (Atiyeh & Duvnjak, 2005) with a reduction of AC after membrane separation

on a comparable solution. It could not be concluded if filtration after AC treatment improves decolourization since it is unclear if pigments that would be filtered are already adsorbed by AC.

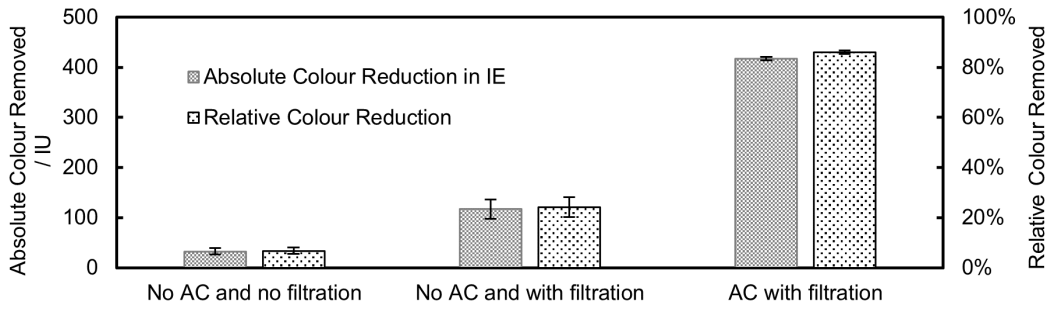

Figure 3: Colour removed due to filtration compared to colour removed due to AC for dilution to 30 Brix and Ac dosage of 0.6 g / 100 ml

3.3 Adsorption Isotherms

Langmuir and Freundlich model showed a good fit for the datasets with a coefficient of determination values $R^2 > 0.95$; see Table 3. The negative Langmuir equation parameters are against physical logic. Thus, the present adsorption mechanism does not meet approaches from the Langmuir model but fits the multilayer Freundlich adsorption very well. The linear behaviour, as presented in Figure 4, isotherms are more convex for higher dilutions and are approx. linear for 30 and 40 Brix concentrations, which means higher dilutions are a more unfavourable isotherm (Weber & Edward Smith, 1987). The same could be read out of the Freundlich parameters where K_f increases with the sugar and thus colour concentration, which means higher adsorbent loading (Worch, 2021). The exponent n_f, which describes the heterogeneity of the adsorbent surface (Worch, 2021), is closer to 1 with higher concentrations. Therefore, the curve is more linear, which means higher adsorbent loadings at lower adsorbate concentrations.

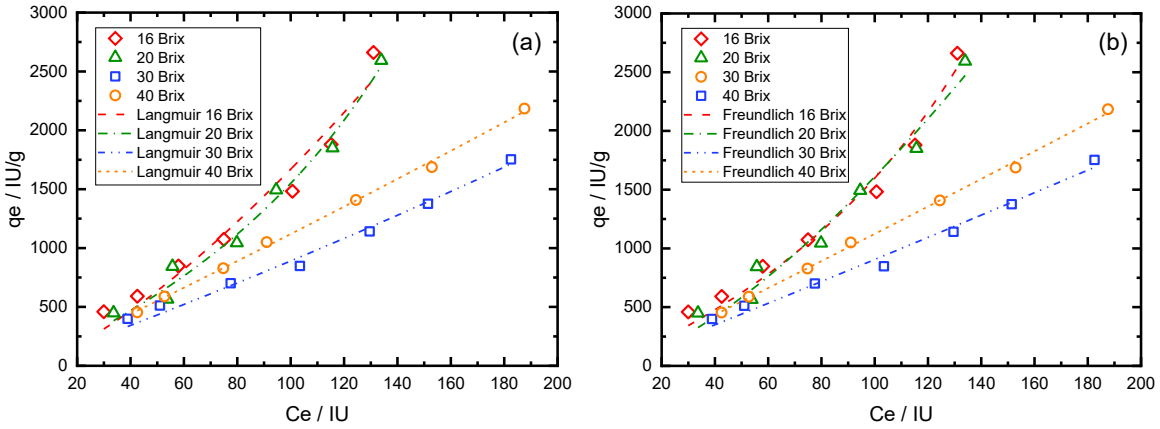

Figure 4: Non-linear fit of Langmuir isotherm in (a) and Freundlich isotherm in (b)

Table 3: Langmuir and Freundlich parameters

Dilution	Langmuir			Freundlich		
	q_{max} / IU·g^{-1}	K_L / IU^{-1}	R^2	K_f / g^{-1}	n_f	R^2
16 Brix	-2821	$-3.62 \cdot 10^{-23}$	0.9783	2.754	1.391	0.9590
20 Brix	-2849	$-3.52 \cdot 10^{-03}$	0.9829	1.877	1.467	0.9729
30 Brix	-14122	$-5.93 \cdot 10^{-04}$	0.9873	7.608	1.038	0.9851
40 Brix	-35404	$-3.06 \cdot 10^{-04}$	0.9979	9.611	1.034	0.9978

4. Conclusions

Decolourization by AC adsorption proved to be a highly suitable method. It was shown that colour removal of about 85 % to 90 % was possible, which led to a colourless product (colour of nearly 50 IU). Optimal process conditions in terms of adsorption time were high dilution and AC dosage, which on the other hand, leads to

increased use of water, energy and AC. Determination of optimum dosages and adsorption isotherms showed that low dilutions and, thus, high colour concentrations are favourable for efficient use and reduction of AC. Thus, for the determination of the optimum process conditions, the relationship between faster adsorption with higher water and energy consumption and lower dilution for less required AC needs to be considered in further investigation.It was demonstrated that filtration of glucose syrup also shows significant removal of colour. Therefore, pre-treatment by filtration, such as microfiltration or ultrafiltration, could be a promising technology for the partial reduction of resources, especially AC. For a better understanding, additional studies in this field are required.

Nomenclature

A – Absorbance at wavelength of 420 nm
b – length of absorbing bath in cm
c – concentration of total solids g/L
C_e – adsorbate concentration in fluid in IU
K_f – Freundlich konstant in g^{-1}
K_L – Langmuir konstant in IU^{-1}
n_f – Freundlich exponent
q_e – adsorbate concentration on the solid in IU/g
q_{max} – maximum adsorbed adsorbate in IU/g

Acknowledgements

The authors acknowledge financial support through the COMET Centre CHASE. Funded within the COMET − Competence Centers for Excellent Technologies programme by the BMK. the BMDW and the Federal Provinces of Upper Austria and Vienna. The COMET programme is managed by the Austrian Research Promotion Agency (FFG). This project has also received the collaboration of Vienna University of Technology and AGRANA Research & Innovation Centre as an industrial partner.

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