Decolourisation of a Pulp Mill Effluent using Commercial Activated Carbons

João Valente Nabais[1], Peter Carrott, M.M.L. Ribeiro Carrott, Liliana Marques
[1]Universidade de Évora, Departamento de Química e Centro de Química de Évora,
Rua Romão Ramalho, 59, 7000 Évora, Portugal.
Email: jvn@uevora.pt

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INTRODUCTION

The decolourisation of industry effluents is a challenging and fundamental task related to pollution control, mainly in pulp mill and textile industries. The dark colour of the pulp mill effluent, depending on the river characteristics, can lead to the reduction of the light penetration into the aquatic environment with the consequent decrease of photosynthesis and aquatic life destruction. Also, the lignocelulosic material deposited on the margins and river bed can lead to a large depletion of the dissolved oxygen with the creation of anaerobic conditions that can give rise to the death of aquatic organisms (Ali, 2001).

The chemical composition of the pulp mill effluent (referred as effluent) is very complex. Nevertheless, we can say that the lignin and tannin compounds are the main causes for the effluent´s dark brown colour. Among these compounds we can find hidroxyphenyl, siringyl and guaiacyl complexes (Mohan, 1997). These compounds are chemically stable, resistant to biodegradation and extremely difficult to separate by most methods in cost effective processes, such as membrane adsorption (Mutlu, 2002), cationic coagulants, ultrafiltration (Mutlu, 2002) and chemical oxidation (Malik, 2004). One of the most promising methods is the use of activated carbons for the removal of the effluent colour.

In this work the use of 5 commercial activated samples with different shapes, origins and characteristics were tested for the decolourisation of a pulp mill effluent collected directly on the effluent discharge of a plant situated in Setúbal, Portugal, property of Portucel. The colour adsorption was done using batch and dynamic trials.

EXPERIMENTAL

Carbon materials

The activated carbon samples used were Norit Azo A-5288 (AZO), Merck granular, Cat. Nº 102518 (MERCK), DCL GDC 753 from Sutcliffe Speakman (DCL) and X2MH 6/8 from Takeda (X2MH).

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[1] Author to whom any correspondence should be addressed.

Characterisation

The activated carbon samples were characterized by FTIR, mass titrations, nitrogen adsorption isotherms at 77K, elemental analysis for oxygen content, acid-base titrations, iodine index and methylene blue index.

Liquid phase adsorption

The colour removal was tested through batch trials by the contact of the activated carbon samples with the effluent at 25ºC for 24h in a stirring thermostated bath using 50mL of effluent and different masses of activated carbon. Also, column adsorption experiments were used. In this case glass columns with 12.5 to 16.0cm length and 7.75 to 14.4cm diameter filled with activated carbons were used. The effluent had a bottom up flow through the column. The effluent colour was determined by Uv-Vis spectrophotometry at 400nm. Additionally, the effluent AOX, total organic mater and N and P concentration before and after the contact with the activated carbons were determined.

RESULTS AND DISCUSSION

Carbon materials characterisation

Chemical characterisation

The point of zero charge (pzc) values determined by mass titration and the estimate of the concentration of acidic and basic functional groups made from the acid-base titrations are shown in table 1. As can be seen, despite all samples having basic properties, with pzc between 9 and 11, the acidic and basic concentration of the functional groups is somewhat different for each sample which indicates that the chemistry is also different. This fact is also proven by the FTIR analysis. Likewise, the iodine and methylene blue adsorption capacity indicated respectively by the iodine and methylene blue index is quite different among samples. We must note that the methylene blue index is the K value obtained from the Freundlich equation applied to the adsorption data.

TABLE 1: Activated carbon chemical characteristics.

Sample	Group concentration / $mmolg^{-1}$		pzc	% (w/w) O	Methylene blue index /$molg^{-1}$	Iodine index / mgg^{-1}
	Acidic	Basic				
AZO	0.714	1.420	10.87	5.50	0.344	957
X2MH	0.335	0.667	9.62	3.56	$1.5x10^{-9}$	108
DCL	1.145	0.599	10.36	2.52	0.080	651
MERCK	0.671	0.562	10.20	3.69	0.042	970

Textural characterisation

The nitrogen adsorption isotherms at 77K, not shown here, revealed different behaviour which indicates activated carbons with somewhat different porosity (Rouquerol, 1994), as can be seen in table 2. X2MH is the sample with more closed porosity, whereas DCL and MERCK samples possess the highest values for total pore volume, V_S. The maximum apparent surface area (S_{BET}) is obtained for AZO and MERCK. We can also note that X2MH has more uniform porosity than other samples with the presence of small micropores indicated by the similar values calculated for V_S and V_0 . In contrast, the porosity of DCL and MERCK samples range from small to larger micropores or small mesopores.

TABLE 2: Textural characterisation of the carbon samples by analysis of nitrogen adsorption isotherms at 77K.

Sample	α_S method		BET method	Dubinin-Radushkevich method	
	V_S / cm^3g^{-1}	S_{ext} / m^2g^{-1}	S_{BET} / m^2g^{-1}	V_0 / cm^3g^{-1}	E_0 / $Kjmol^{-1}$
AZO	0.30	276	957	0.38	22.3
X2MH	0.24	13	541	0.24	28.6
DCL	0.41	94	900	0.35	20.3
MERCK	0.42	71	980	0.38	21.5

Adsorption studies

Batch tests

The colour removal isotherms at 25ºC are shown in figure 1. The best activated carbons tested are AZO and MERCK that reache 95% and 90% colour removal at 3% (w/v) carbon dosage, respectively. DCL sample can remove about 70% of the initial effluent colour. On the other hand, X2MH sample only achieve 30% at 5 % carbon dosage. According to the Giles classification (Giles, 1960) the isotherms are all different since AZO can be classified as "High Afinity", Merck as "Langmuir", DCL as "Freundlich" and X2MH as "Sigmoidal".

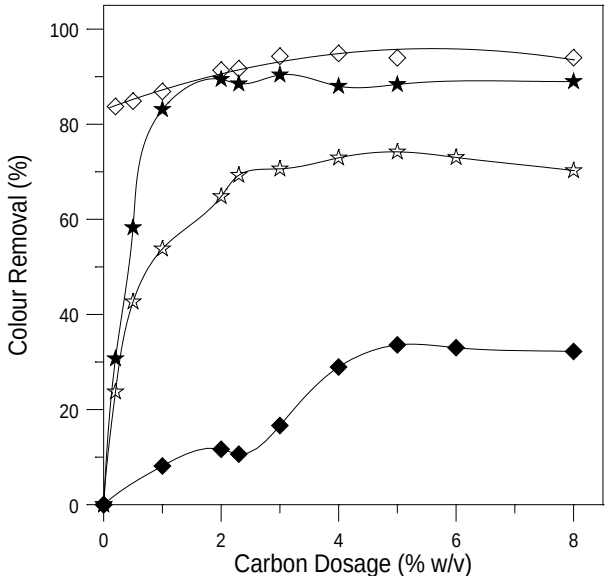

FIGURE 1: Colour removal isotherms at 77K. ◊ AZO ◆ X2MH ✯ DCL ★ MERCK.

In order to identify the properties that have impact on the carbon ability to perform the effluent decolourisation we plot the colour removal at 5 %(w/v) versus iodine index, methylene blue index, acidic and basic groups concentration, S_{BET}, pzc, V_S and V_0, plots shown in figure 2. First of all we note that the methylene blue index is useless for the prediction of effluent colour removal ability (plot not shown here) because we could not find any type of correlation between those two parameters. The same conclusion can be drawn for the V_S influence.

The analysis of figure 2 lead to the following conclusions:

- Iodine index can be used as a guide for the effluent colour removal efficiency.

- Acidic groups are more important than the basic groups on the adsorption mechanisms involved in the activated carbon adsorption of the chemical species that gave colour to the effluent.
- The colour removal is proportional to the pzc and V_0 samples values.
- For small values of S_{BET} this parameter has a significant impact on the colour removal but for sample with S_{BET} bigger than $900 m^2 g^{-1}$ the colour removal is apparently independent of the BET surface area.

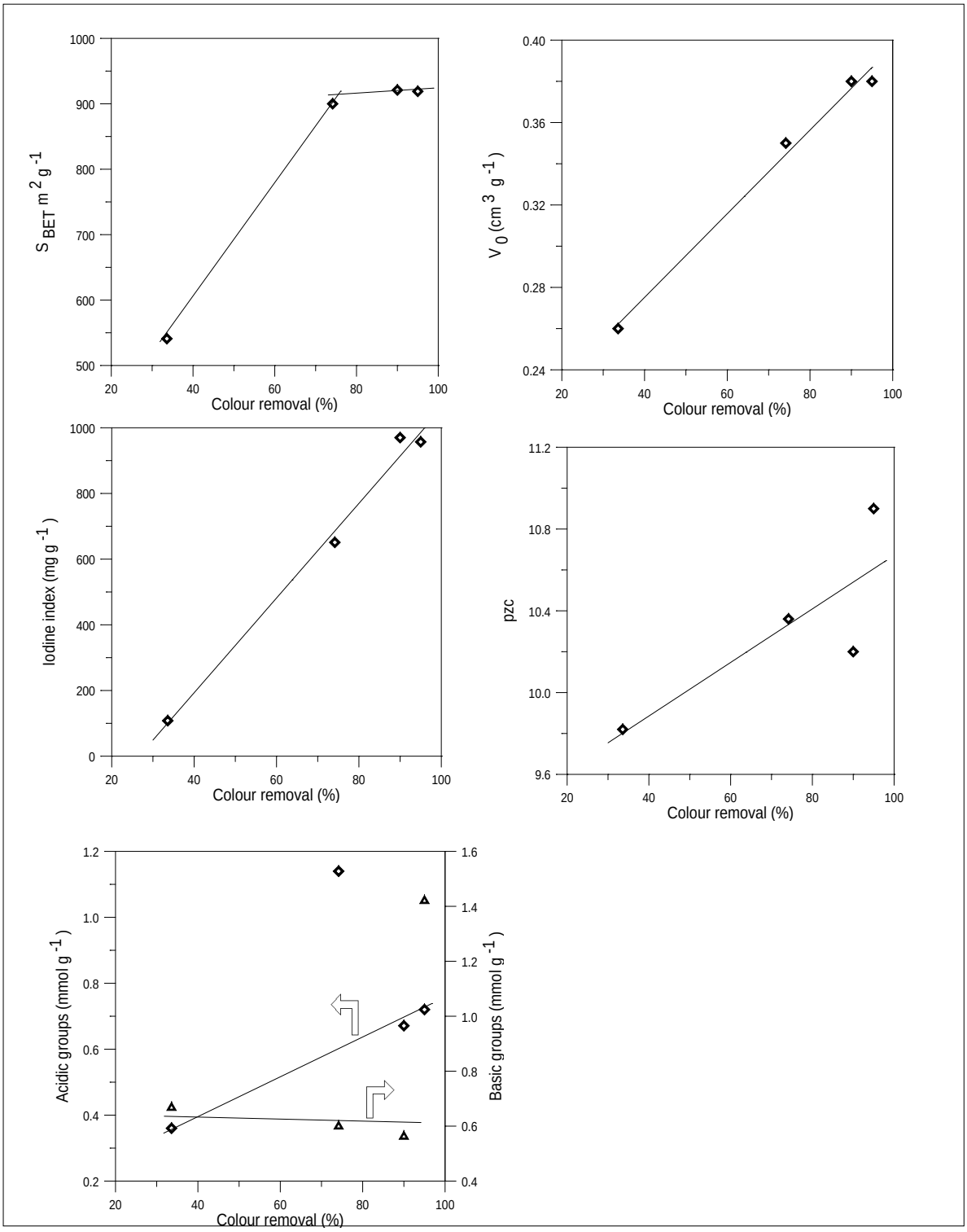

FIGURE 2: Colour removal at 5 %(w/v) versus iodine index , acidic and basic groups concentration, S_{BET}, pzc, V_S and V_0

The effluent contact with activated carbon samples also has a positive impact on other effluent characteristics like the total amount of halogenated organic compounds (AOX), nitrogen content and total organic content (TOC), as can be seen in figure 3. Also, we can note that the phosphorous content is unaltered after the activated carbon adsorption.

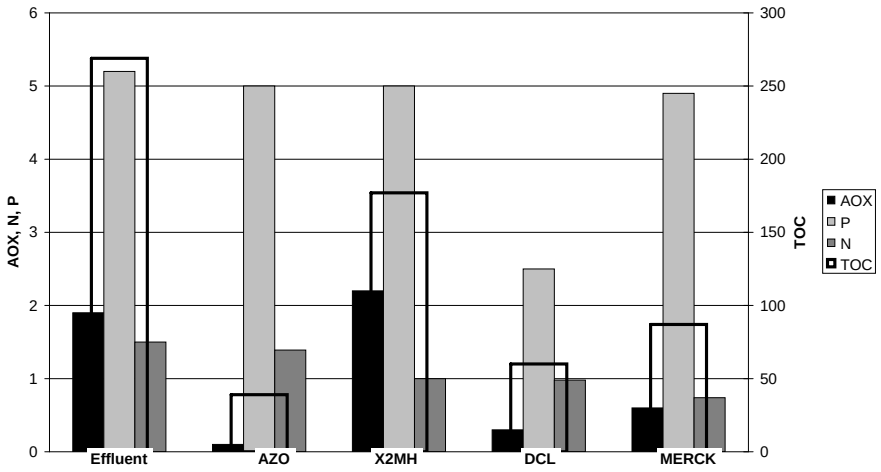

FIGURE 3: Impact of the activated carbon adsorption on other parameters.

Column tests

The column tests performed with X2MH, DCL and MERCK samples showed that we can obtain similar results as in batch tests, as expected. The breakthrough curves, not shown here, reveal that X2MH sample has a very fast saturation while DCL and MERCK sample have good efficiency with 90% colour removal when the effluent volume that passes through the column is 10 and 20 times the activated carbon volume, respectively.

CONCLUSIONS

1) The activated carbons AZO and MERCK can be used for the decolourisation of the pulp mill effluent tested.
2) Provide the pores are large enough to allow the adsorption of the pollutants; the colour removal is mainly dependent on the chemical characteristics of the samples.
3) An easy and fast method to predict the colour removal capacity is the iodine index. For this propose the methylene blue index is useless.
4) The activated carbon adsorption increment the effluent quality by promoting the decrease in other parameters like AOX and TOC.

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