Fast determination of anionic groups in different pulp fibers by methylene blue sorption

PEDRO FARDIM AND BJARNE HOLMBOM

ABSTRACT: Methylene blue (MB) sorption can be used to determine anionic groups (AGs) in chemical, chemimechanical, and mechanical pulps. Fast sorption performed in 5 min under vigorous agitation gave similar results as obtained using 20 h sorption time, with no observed effects of AG counter ions. The MB sorption isotherm showed different plateaus according to the amount of free MB in solution. We also identified regions related to chemisorption and physisorption. For analytical purposes, the saturation level in the chemisorption process must be the target for performing MB sorption. The isotherm in the chemisorption region for this study was of the Langmuir type, according to experimental data fitting and as observed by X-ray photoelectron spectroscopy (XPS) analyses. Based on our results, we suggest that pulp and paper mills can use MB sorption as a fast and reliable method applied to "on-line" and "at-line" process control.

Application: Anionic groups in pulps can be determined for process control in pulp and paper mills using "at-line" or "on-line" conditions.

Pulping, paper manufacturing, and converting involve a multitude of bulk and surface chemical interactions important to product consolidation and performance [1]. The anionic (acidic) groups (AGs) in fibers make a special contribution to these interactions due to their ion exchange capacity at papermaking conditions. They can interact with retention aid polymers, contributing to floc formation and stability. Their interaction with metals can promote fiber wall swelling, affecting the adhesion and accessibility of colloidal particles [2, 3], beating response, and strength properties [4-6].

The total amount of AGs in pulp fibers depends on the wood used as raw material, and on chemical reactions and dissolution of fiber components in the processes used for pulping and bleaching. AGs in fibers either originate from the wood or form in pulping or bleaching processes. AGs that originate from wood are generally associated with the hemicellulosic or pectic components. They can be in hydrogen, salt, or ester form, as lactones or methyl esters, for example.

Various AGs can form during pulping. Conversion of 4-*O*-methyl glucuronic acid to hexenuronic acid has been reported, as has removal of uronic acid groups in chemical pulping, elemental chlorine free (ECF) bleaching, and totally chlorine free (TCF) bleaching [7]. Carboxyl groups can form in the residual lignin in kraft cooking, while sulfonic acid groups are added to lignin in chemithermomechanical pulp (CTMP) and sulfite pulping processes. Alkaline treatment of mechanical pulps can give methyl ester cleavage and exposure of galacturonic acid groups in pectin, increasing the AG amount dramatically [8]. Oxidative bleaching sequences can also generate carboxyl groups in lignin in CTMP and TMP pulps [9] and in cellulose or hemicelluloses in kraft pulps.

In papermaking conditions, wood-originating components such as extractives and hemicelluloses can be released into the process waters to yield dissolved and colloidal substances in the liquid media [10]. During paper sheet formation and removal of water, these components can deposit on the fiber surface, further increasing the amount of AGs [11].

Various laboratory methods are effective in determining AGs. Conductometric and potentiometric titrations with sodium hydroxide (NaOH) are commonly applied [12-14]. However, they require proper sample pretreatment to convert AGs to their protonated form. Both methods are very time-consuming because they require a few minutes equilibration between additions of base aliquots. Another method for AG determination is polyelectrolyte adsorption [15], but it is laborious and time-consuming, and it gives higher values than conductometric titrations [16]. In contrast, methylene blue (MB) sorption, based on the replacement of AG counter ions by the cationic dye, has been reported to be a straightforward and repeatable method [16-18]. However, the usually applied MB sorption time of 20 h excludes its use for process control in pulp and paper mills.

Pulping, bleaching, and papermaking are dynamic processes traditionally monitored using "off-line" analysis. This limitation is due to the complex nature of pulp and paper samples requiring specific pretreatments, conditioning, or separation before analysis. In the work presented here, we describe a fast method for determination of AGs through MB sorption that can be used for "at-line" or "on-line" analysis in pulp and paper mills.

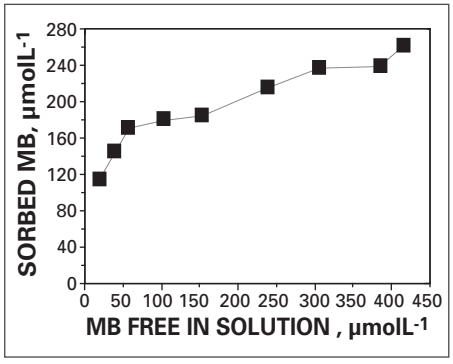
EXPERIMENTAL SECTION

Pulps

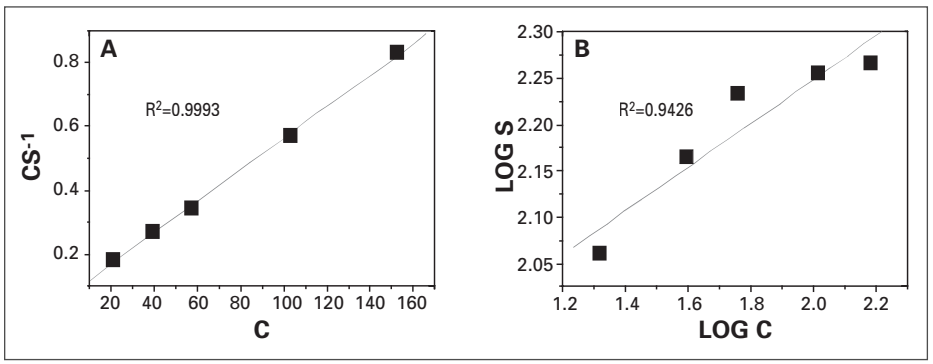
For our experiments, we obtained a broad selection of pulps comprising bleached and unbleached kraft, mechanical, and chemimechanical pulps from Finnish and Brazilian pulp mills. All pulps were washed with distilled water at 60°C and extracted with acetone-water (90:10 v/v) to remove dissolved and colloidal substances and extractives. Metal ions were removed by treating with 0.01 M EDTA and 0.01 M hydrochloric acid (HCl) and subsequent washing with deionized water until the conductivity of the filtrate was lower than 2 μScm^{-1}.

Conversion of AG to sodium and calcium forms

We converted a peroxide-bleached mechanical pulp to sodium and calcium forms of AGs by treatment with 1 mM NaOH and 1 mM calcium chloride ($CaCl_2$) solutions, respectively. We treated the pulp sample three times with each solution at 1% consistency by stirring for 30 min followed by filtration. Then the pulps were washed with deionized water



1. The MB sorption isotherm for a PBTMP sample using 20 h reaction time. Two different saturation levels are observed at concentrations of free MB in solution between 60-150 µmolL^{-1} and 300-400 µmolL^{-1}, respectively.



2. Treatment of MB sorption experimental data according to Langmuir (A) and Freundlich (B) isotherms. Data fits better to a Langmuir isotherm.

until the conductivity of the filtrate was lower than 2 µScm^{-1}.

MB sorption

About 100 mg of o.d. pulp was transferred to a 50 mL mixing flask, weighed and mixed with a proper volume of a solution of 0.4 mM methylene blue, preprepared in 0.60 mM barbital buffer (pH 7.8). We adjusted the volume of the MB solution according to the total amount of AGs in a way that 50% remained free in solution. This volume was varied for a peroxide-bleached mechanical pulp in order to obtain a sorption isotherm. The reaction time for this sample varied between 5 min and 20 h. We studied other samples limited to a 5-min reaction time, but the volume of MB solution was adjusted in a way that the concentration of free MB after sorption was approximately 100 µmolL^{-1}. All pulp samples were vigorously stirred (500 rpm) during the reaction time and then filtered using a sintered glass filter. A blank determination without pulp was performed. We measured the recovered filtrate by UV-visible spectroscopy, at a wavelength of 664 nm. We simultaneously made a calibration curve by using the 0.4 mM methylene blue solution diluted at a ratio of 25:250, using 0.6 mM barbital solution. Each sample and blank filtrate was diluted 25 times in the same way before absorbance measurement. The calculation of AG content incorporated the o.d. weights of the pulp samples and blank value [17, 18].

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were recorded in low resolution mode using a Physical Electronics Quantum 2000 ESCA instrument, equipped with a monochromatic AlKα X-ray source, operated at 25 W power. The photoelectron collection was at 45° in relation to the sample surface and the spot size had a diameter of 100 µm. We measured at least three different spots on each sample to determine the analytical error. The pass energy was 117.4 eV and charge compensation was performed using a combination of an ion gun bombarding (5 eV Ar^+ ions) and a low energy electron flood gun. XPS measurements were performed only on the samples of the sorption isotherm.

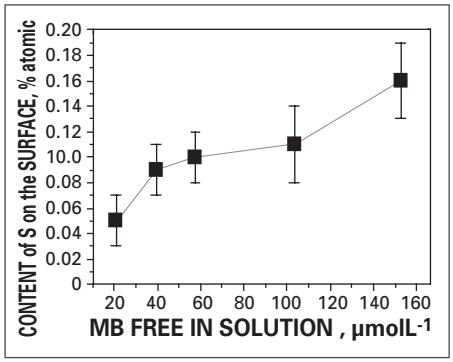
RESULTS AND DISCUSSION

Interaction between MB and AG

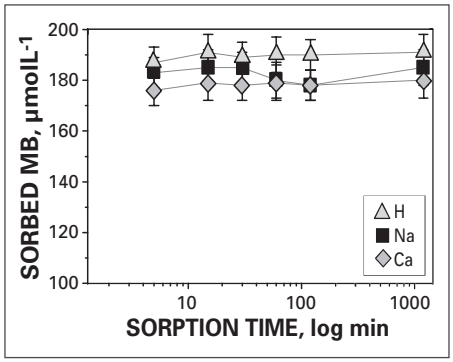
We studied the interactions between MB and AGs for a peroxide-bleached thermomechanical pulp (PBTMP). We obtained a sorption isotherm by varying the amount of dye in solution for pulp with the anionic groups in their H-form (**Fig. 1**). The reaction time was 20 h. Different saturation levels occurred in this isotherm as a function of the amount of free dye. The first saturation level occurred between 60 and 150 µmol/L of free dye concentration, the second at 300-400 µmol/L. The amount of MB sorbed at the first saturation level was the same as the value obtained by conductometric titration to this sample [16]. We believe the MB cations neutralize the AGs at the first saturation level, following an ion-exchange reaction. We associate the second saturation level with sorption onto hydroxyl groups present in cellulose and hemicelluloses. Similar sorption mechanisms have been proposed for cotton linters [17]. Another possibility for this increase in sorption may be the formation of MB multilayers, since the isotherm shape is similar to that observed for a Brunauer, Emmett, and Teller (BET) isotherm.

Results have shown that the interaction between pulp fibers and the dye are not exclusively governed by electrostatic forces due to ion-exchange reaction, but additional factors such as affinity, hydrogen bonding, and van der Waals and hydrophobic forces must be taken into account. Another important indication from the isotherm is that these interactions are dependent upon the MB concentration. An ion-exchange reaction that makes the sorption suitable for analytical purposes is achieved if, at equilibrium, an approximate free dye concentration of 100 µmolL^{-1} is obtained. If a free dye concentration higher than that, we expect hydrogen bonding involving carbohydrate hydroxyl groups. Other attraction forces weaker than hydrogen bonding, such as van der Waals and hydrophobic ones, may also occur. The van der Waals interactions involve attractions of the delocalized π electron system of the double bonds in the MB molecule with the positively charged nucleus of the atoms in the pulp macromolecules. The hydrophobic forces, which are much weaker than van der Waals interaction, stem from the attraction between the hydrophobic parts of the dye molecule and hydrophobic regions on the fiber [19]. We do no expect the latter for MB due to the absence of alkyl chains in the molecule, which could contribute to a hydrophobic character. The van der Waals forces can also contribute to multilayer sorption once that attraction can occur between a sorbed and a non-sorbed MB molecule.

Note that sorption isotherms are empirical and a proper theoretical treatment, even for a gas-on-solid process, still has many limitations. In the case of sorption from solution, as studied here,



3. Atomic concentration of S measured by XPS as a function of the concentration of free MB in solution for the PBTMP sample.



4. Effects of time and H, Na, and Ca as AG counter ions on the MB sorption of a PBTMP sample.

effects of solvent molecules and heterogeneity of the fibers are complex factors that make a theoretical treatment more difficult. However, if we take a qualitative approach, we can divide the MB sorption isotherm into two distinct regions with characteristic interactions, depending on the concentration of free dye in solution at equilibrium. We attribute the region between zero and 100 µmolL^{-1} to a chemisorption process driven by the ion-exchange reaction and formation of ionic bonds between AG and MB cations. The region above 100 µmolL^{-1} seems due to a physisorption process driven by hydrogen bonding, van der Waals attraction, and hydrophobic forces.

We treated the experimental data in the region concerning the chemisorption according to Langmuir and Freundlich isotherms to evaluate whether favorable anionic sites are occupied first by MB cations (**Fig. 2**). The Langmuir isotherm is based on independence and equivalence of sorption sites, while the Freundlich isotherm can take heterogeneity into account. Both are empirical treatments and the Freundlich is often used for sorption in liquid media.

According to the R-squares we obtained (Fig. 2), the Langmuir isotherm fits the experimental data much better in the chemisorption region than does the Freundlich isotherm. This result suggests that the energy of sorption is constant, the number of binding sites is finite, and the surfaces accessible to the MB cations are flat at molecular level. These considerations seem surprising on first view, especially considering that the peroxide-bleached mechanical pulp has different AGs situated at both carbohydrates and lignin. The consideration of finite binding sites is reasonable, but those relating the surface flatness in water and the sorption energy are difficult to explain. Perhaps a strong affinity between the dye and the anionic groups can affect these parameters, but little is known about this property.

We used XPS to investigate the effects of MB sorption on the external surface composition. Atomic concentration of sulfur, which has a high elemental sensitivity in this technique, was measured on samples with different amounts of MB sorbed (**Fig. 3**). Though not observed in the original pulp sample composition, sulfur is present in the MB molecule. Results have shown that surface coverage is achieved at the same chemisorption region as observed in the MB isotherm (Fig. 1). This is another indication of a Langmuir behavior during the ion-exchange process.

Another important parameter in the interaction between MB and the pulp fibers is the pH. The sorption pH is maintained at about 7.8 by a buffer system in order to have the pulp AGs predominantly in their ionized form. It also neutralizes the H^+ ions, which can reduce the sorption by competition for the same anionic sites. After dye sorption, the buffered medium had a pH of 7.3 due to release of H^+ ions from the pulp and subsequent neutralization. We did not observe competition from Na^+ ions present in the buffer system here.

Effects of time and anionic group counter ion on MB sorption

The reaction time did not affect the sorption of MB onto a PBTMP sample with anionic groups on its H-form (**Fig. 4**). We vigorously mixed the pulp with the MB solution and results obtained at 5 min sorption time were similar as those observed at 20 h, considering the deviations in the measurements. This result is different from a previous work using cotton linter [17]. This may have been due to the higher porosity of the spruce pulp fibers in comparison with cotton fibers. Mixing can also contribute to the diffusion rate of cations through the fiber wall. It must also be made clear that such a fast ion exchange can not be observed even for ions smaller than MB cations and long equilibrium times are needed, for example in conductometric titrations or magnesium (Mg) exchange. This consideration may also indicate that the MB ions have a strong affinity to pulp fibers and that this parameter has an important—and not much investigated—role.

We also studied the effects of different AG counter ions other than H^+. The H^+ ions were replaced by calcium and sodium and the MB sorption was performed for different reaction times (Fig. 4). No significant effect of time was observed. We observed very low differences between different counter ions, indicating that the MB cations can replace both sodium and calcium without considerable competition. These counter ions were chosen because they are usually present in pulps, being introduced during pulping and bleaching operations. The reaction time of 5 min can also be used for pulps in calcium and sodium forms, thus it seems that a sample pre-treatment with acid can be left out without any substantial effect on the AG determination.

Fast determination of AG in different pulp samples

A broad selection of pulps was analyzed by a rapid MB sorption method with a reaction time of 5 min. Results were compared with the conductometric titration and 20 hours MB sorption data obtained in the previous work in other laboratories using the same samples [16]. All studied samples exhibited similar results, indicating that the short sorption time is applicable with good repeatability (**Table I**).

The repeatability in the fast method appeared slightly lower than in the conventional MB sorption. The similarity in results using the fast and the conventional MB sorption methods observed for mechanical pulps were to a certain

extent surprising. In the case of polyelectrolytes, the penetration and diffusion through the fiber wall can take up to 2 h for mechanical pulps and about 30 min for chemical pulps. Conductometric and potentiometric titrations are good examples of time dependence to reach equilibrium conditions. Mechanical pulps usually require a long time between base aliquot additions in these techniques. On the other hand, it seemed that the MB sorption under vigorous agitation was a versatile, simple, and reliable technique to quantify AGs.

Perspectives for application of fast MB sorption in process control

Determination of AGs for process control is of great interest because this parameter has an important influence in pulp and paper manufacture. The methods available are tedious and time-consuming and sometimes far from the reality and needs of the industry. Methods such as conductometric and potentiometric titration require a proper sample pretreatment with acid and a nitrogen atmosphere during the determination, which limits the application to the laboratory.

Fast MB sorption may be applied for process control in both "at-line" and "on-line" conditions. Mills could mount a simple workstation close to the digester to monitor pulping using "at-line" conditions. The same concept works for monitoring bleaching and stock preparation. This easily implemented "at-line" workstation would not require high investment. For "on-line" conditions, a suitable device would need to be developed. This "on-line" analyzer needs to extract a sample from the process, remove the water, and mix the sample with the MB solution under agitation for 5 min. The dispersion would then be filtered and the filtrate collected or transferred to a spectrophometric cell to measure the absorbance. Calibration is achieved by using MB solutions with different concentrations. Application of "on-line" measurements presently requires more investment than "at-line," but its use tends to be much more attractive if a commercial analyzer is made available.

CONCLUSION

MB sorption can be used for fast determination of total anionic group content in different pulps. Counter ions usually present in pulps do not influence the measurement. Fast determinations can be performed in "at-line" and "on-line" modes. An "at-line" workstation can be readily implemented while an "on-line" analyzer may be developed. The interaction between MB and fibers is mainly due to an initial chemisorption where the AG is neutralized by an ion-exchange reaction, being followed by a physisorption which must be avoided in analytical determinations. The chemisorption seems to be described by a Langmuir isotherm rather than a Freundlich isotherm. MB seems to have a high affinity to AGs, and vigorous agitation during sorption makes fast determinations feasible if the concentration of free MB is near 100 $\mu molL^{-1}$. **TJ**

Pulps	Fast MB Sorption	Conventional MB Sorption	Conductometric Titration
UBK			
Birch	130 ± 6	115 ± 3	124 ± 2
Pine	81 ± 3	81 ± 2	79 ± 2
Eucalypt	113 ± 11	104 ± 5	105 ± 3
BK-TCF			
Birch	64 ± 5	68 ± 3	66 ± 3
Pine	43 ± 6	45 ± 1	45 ± 1
BK-ECF			
Birch	68 ± 5	65 ± 1	65 ± 2
Pine	38 ± 4	37 ± 1	40 ± 2
Eucalypt	80 ± 1	77 ± 1	83 ± 2
TMP			
UB Spruce	96 ± 5	92 ± 1	87 ± 1
PB Spruce	183 ± 7	178 ± 5	178 ± 6
AT Spruce	157 ± 3	140 ± 10	136 ± 2
CTMP			
PB Spruce	204 ± 10	188 ± 12	187 ± 6
PB Aspen	206 ± 5	211 ± 2	186 ± 5

I. Total anionic groups in different pulps determined by fast MB sorption, conventional MB sorption and conductometric titration [16].

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INSIGHTS FROM THE AUTHORS

We chose to investigate this topic because AGs are essential functional groups in fibers used for papermaking. Most of the paper chemicals that attach to these groups are cationic. AGs are also important to fiber-to-fiber bonding, swelling, and strength properties.

In 2002, we found that MB sorption using 20 hours of sorption time gave similar results as conductometric and potentiometric titrations for a broad selection of pulps. In this work, we have found that only 5 min is needed for MB sorption under proper agitation.

The most difficult aspect of this research was to determine the optimum agitation speeds. The use of a set of pulps very well characterized in chemical composition and AG content played a key role in addressing the optimized conditions.

One must never forget that excellent research has been done in the past and we cannot find that flying through the Internet. The most interesting thing that we found through this study is the short sorption time needed under vigorous agitation. The most surprising thing is that, as far as we know, this had not been discovered before.

The use of this fast method for AG determination can improve process control, especially if an on-line device is used. Usually, mills analyze just a few samples per day due to difficulties in sample pretreatment and the time-consuming methods available. Using fast MB sorption, mills could make several determinations in a very simple way.

Our next step is to develop an on-line device for process control and investigate why MB has such affinity for AGs. MB seems also to be a very good molecular probe for imaging of fiber and paper surfaces.

Fardim and Holmbom are with Åbo Akademi University, Process Chemistry Group, Porthansgatan 3, FIN-20500, Turku/Åbo, Finland, email Fardim at pfardim@abo.fi, Holmbom at bholmbom@abo.fi.

Fardim

Holmbom