



Adsorption of dyes on to cellulose

Sudarath Veravong

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THESE

pour obtenir le grade de

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par

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le **28 mai 2008**

Contribution à l'étude des phénomènes d'adsorption de colorant par les fibres cellulosiques
papetières : cas particulier de bleu méthylène

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INTRODUCTION

Les groupements carboxyliques que contiennent les hémicelluloses ainsi que l'oxydation de la cellulose et de la lignine durant les différentes étapes de cuisson et de blanchiment, sont à l'origine des charges anioniques que contiennent les fibres lignocellulosiques utilisées pour fabriquer le papier. La quantité de ces charges est un facteur déterminant des propriétés physicochimiques des ces fibres ainsi que des propriétés mécaniques des papiers fabriqués à partir de ces matériaux. En effet, c'est de ce paramètre que dépendent les interactions avec les additifs cationiques dans le procédé de fabrication de papier et qui gouverne la capacité d'adsorption des fibres.

Il y a plusieurs méthodes pour déterminer les groupements carboxyliques. La méthode de bleu de méthylène est la plus courante pour de faibles quantités de carboxyle en cellulose. La charge cationique de ce colorant basique, lui permet d'avoir une bonne adsorption sur les fibres cellulosesiques et une bonne interaction avec ses charges anioniques.

Dans ce travail nous nous sommes intéressés à l'étude des phénomènes d'adsorption des fibres de cellulose en présence de bleu de méthylène comme colorant et des propriétés électrocinétiques et du Poly(DADMAC) comme polyélectrolyte. A cet effet, nous avons utilisé la méthode de la spectroscopie UV-Visible pour étudier la phénomène d'adsorption de ce colorant, la mesure du potentiel zêta par la technique du potentiel d'écoulement.

Une partie de ce travail s'est concentrée sur l'étude de l'adsorption de bleu méthylène. Trois types de matière première ont été étudiés : Les pâtes blanchies d'un feuillu (eucalyptus) et d'un résineux (Tarascon) et le coton linters. Ces matières fibreuses ont été traitées mécaniquement à trois niveaux de raffinage même si ceux non raffinage.

Cette étude est partagée sur trois parties :

Dans la première partie nous donnons une révision bibliographique relative aux différents aspects de l'étude.

La deuxième partie est consacrée à une présentation des méthodes et matériels utilisés lors de cette étude.

La troisième partie est consacrée à la discussion de nos résultats ainsi que leurs discussion.

RESUME

1. PARTIE BIBLIOGRAPHIQUE

La feuille de papier est composée essentiellement de fibre d'origine végétale. Le principe de fabrication du papier se base sur la filtration d'une suspension de fibres diluées sur une toile, permettant d'avoir une feuille de cohésion suffisante qui subit, ultérieurement, des opérations de pressage et de séchage.

1.1 Composition chimique du bois

Le bois constitue la matière première la plus utilisée pour la fabrication de la pâte à papier. En allant de l'extérieur vers le cœur du bois, nous distinguons différentes parties, notamment [1] :

- ✓ L'écorce externe (rhytidome) qui joue un rôle de protection du bois.
- ✓ L'écorce interne (liber) qui conduit la sève
- ✓ L'assise génératrice (cambium) qui produit des cellules du bois vers l'intérieur et du liber vers l'extérieur.
- ✓ Le bois proprement dit (xylème) qui se présente sous forme de couches correspondant à la croissance saisonnière et annuelle.

Les fibres de bois sont composées de différentes molécules et macromolécules, qui possèdent des structures et des propriétés chimiques différentes [2].

Ces composées peuvent être classés comme suit :

- ✓ Les hydrates de carbone qui comprennent la cellulose et les hémicellulose.
- ✓ Les substances pectiques.
- ✓ Les substances phénoliques qui comprennent les lignines et les substances colorées.
- ✓ Les résines et les protéines.

1.2 La cellulose

La cellulose est un polymère naturel particulièrement important puisqu'il est le constituant principal de la biomasse végétale. A ce titre, il est produit par dizaines de milliards de tonnes chaque année.

D'un point de vue chimique, la cellulose est un polyholoside dont la composition correspond à la formule $(C_6H_{10}O_5)_n$. Elle est constituée de macromolécules linéaires de haut poids moléculaire ($1,5 \cdot 10^6$ à $2 \cdot 10^6$ g/mol), formées – comme le montre la Figure 1 – par l'enchaînement de motifs glucose liés entre eux par des liaisons β (1-4) ou plus précisément de motifs cellobiose [3].

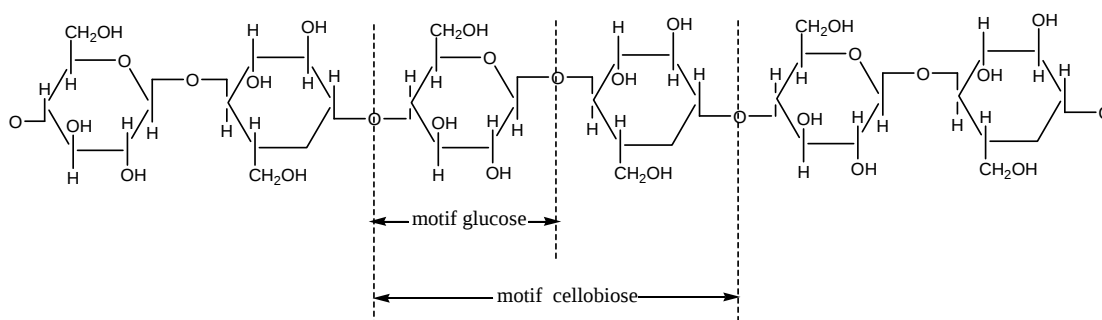


Figure 1 : Chaine cellulosique

Malgré la présence multiple de groupement fonctionnels hautement réactifs que sont les hydroxyles, la cellulose est très peu réactive : elle constitue la composante la plus résistante dans le bois (et la pâte) puisqu'elle est la moins accessible à l'eau et aux produits chimiques vu le degré de cristallinité très élevé et la forte liaison entre les macromolécules [2,4].

La cellulose est une macromolécule très hydrophile, propriété qui est à l'origine, pour les fibres qui en sont tirées (coton, lin, chanvre..., etc.), de leur grand confort en tant que fibres textiles.

La chaîne cellulosique peut contenir quelques motifs de sucre autres que le glucose, principalement du xylose et de l'arabinose. Ces motifs « anormaux » de la chaîne cellulosique induisent des défauts de structure acides permet la coupure des

chaînes cellulosiques en donnant toute une série de produits pouvant aller jusqu'au glucose.

1.3 Les hémicelluloses

Les hémicelluloses sont des hydrates de carbone ayant un degré de polymérisation moyen de 150, composés principalement d'hexoses (glucose, galactose mannose....etc.) et de pentoses (xylose, arabinose...etc.) Elles se caractérisent par leur structure qui est moins régulière que la cellulose à cause de la présence de différentes unités dans leurs chaînes et leur solubilité dans des solutions alcalines diluée [1,3].

Dans la nature, il existe deux grandes catégories d'hémicelluloses ; la première catégorie regroupe les hémicelluloses pratiquement linéaires, de masses molaires élevées et avec peu ou pas de groupements carboxyliques. La deuxième catégorie est caractérisée par des structures ramifiées dont la masse molaire est plus faible et la teneur en fonctions carboxyliques plus forte [1].

Le galactoglucomannane, constitué d'une chaîne linéaire de glucose et de mannoses lié en β (1,4) et substituée en α (1,6) par des motifs de galactose, est le principal constituant (20% de la masse sèche du bois) des hémicelluloses des résineux suivi de l'arabino-(4-O-methylglucurono)xylane (5 à 10%) qui est constitué d'unités de xylose liées entre elles par des liaisons β (1,4) substituées par le L-arabinofuranose et l'acid 4-O-methylglucoronique.

Une grande partie des hémicelluloses du bois de feuillus est composée de glucuronoxylanes (15 à 30% de la masse sèche du bois) ; ce sont des chaînes composées de motifs de D-xylose liés entre eux en β (1,4) et substituées en α (1,2) par l'acid 4-O-methylglucoronique. Le feuillus contient, également, de petites quantités (2 à 5%) de glucomannose (voir Figure 2) composé des unités de glucose et de mannose liées entre elles par des liaison β (1,4) [3].

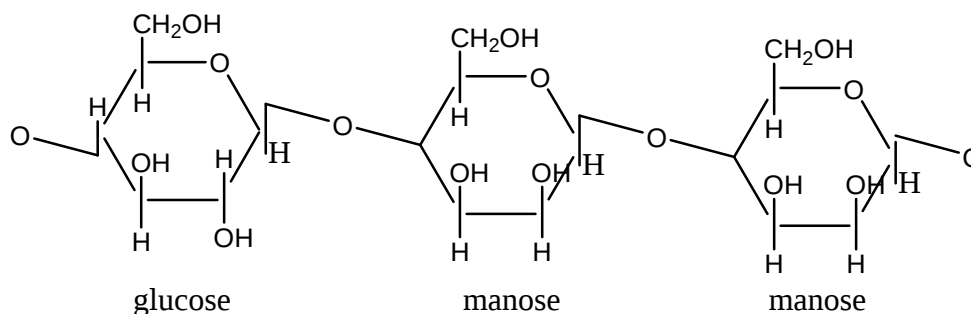


Figure 2 : Exemples des chaînes d'hémicelluloses : glucomannose

Les hémicellulose sont des macromolécules très hydrophiles. Leur présence est indispensable pour la fibre papetière car elles améliorent d'une manière significative les propriétés mécaniques du papier [1].

1.4 Les substances pectiques

La pectine est une autre forme d'hémicellulose. Elle est constituée d'une suite de monomères de dérivés d'oses. Son rôle est de renforcer les parois primaires de la cellule végétale.

La pectine est constituée principalement de polymère d'acide uronique. Les acides uroniques les plus répandus sont l'acide galacturonique et l'acide glucuronique (voir Figure 3) qui sont respectivement les produits de l'oxydation du galactose et du glucose sur leurs fonctions alcool primaire.

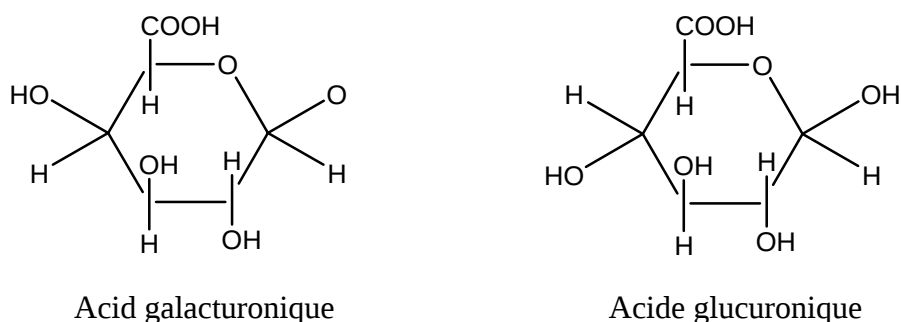


Figure 3 : Exemple de structure chimique de deux acides uroniques

1.5 La lignine

La lignine est après la cellulose, le polymère naturel d'origine végétale le plus présent sur terre. Elle représente entre 17 et 33% de la masse sèche du bois.

La lignine est un polymère aromatique très complexe dont la structure chimique détaillée est difficile à déterminer pour les raisons suivantes [4]:

- ✓ La tridimensionnalité de ce polymère qui, pour son extraction et sa valorisation ultérieure, nécessite une dégradation partielle qu'il est difficile de contrôler.
- ✓ L'extrême complexité de la structure moléculaire qui ne peut être représentée que par une composition moyenne, variable selon les espèces végétales dont elle est extraite.

La lignine originelle n'est pas une substance unique : en plus de la variation suivant les espèces végétales, sa structure est différente selon l'âge des tissus et les conditions climatiques [1].

Les différentes études effectuées sur la structure chimique de la lignine montrent qu'elle est composée de produits qui présentent des analogies chimiques : les groupements gaïcylopropane caractérisent la totalité de la lignine contenue dans la pâte de résineux tandis que la lignine de feuillus se compose des groupements syringylopropane et des groupements gaïcylopropane qui sont représentés par la Figure 4 [3].

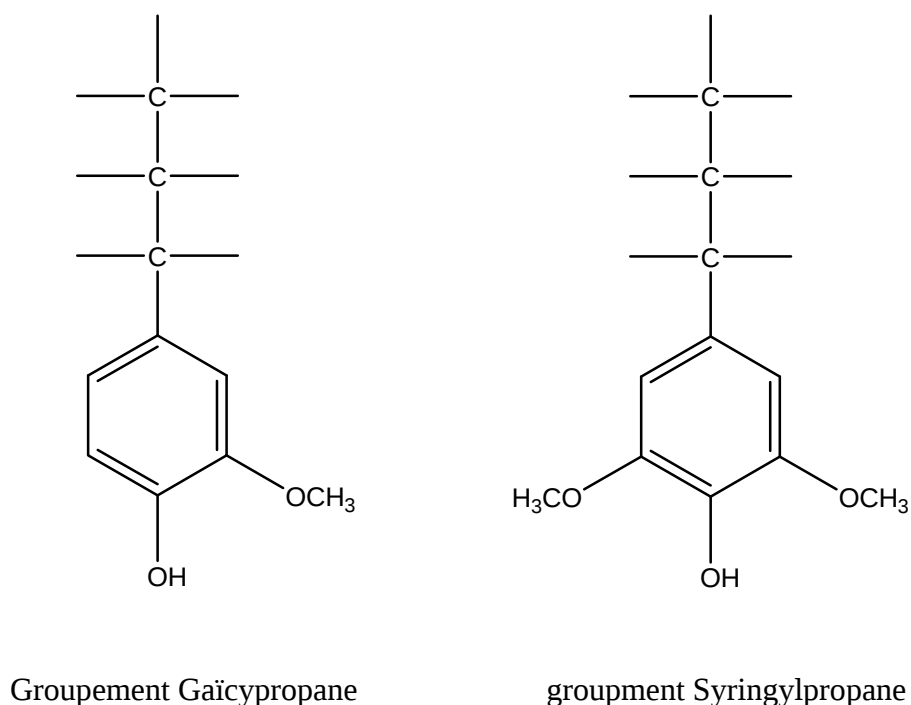


Figure 4 : Exemple de groupements monomères de la lignine.

Les lignines ont, originellement, une couleur blanchâtre mais elles peuvent s'oxyder photo chimiquement pour donner des colorations. C'est la raison pour laquelle il faut les éliminer lors des procédés de fabrication des pâtes à papier [3].

1.6 Les tannins et autres composés phénoliques

Les tannins sont des oligomères phénoliques naturels. Ils sont présents essentiellement dans les écorces du pin et du mimosa. Les deux structures les plus représentatives des tannins sont les flavonoïdes 4-6 et les flavonoïdes 4-8 [3].

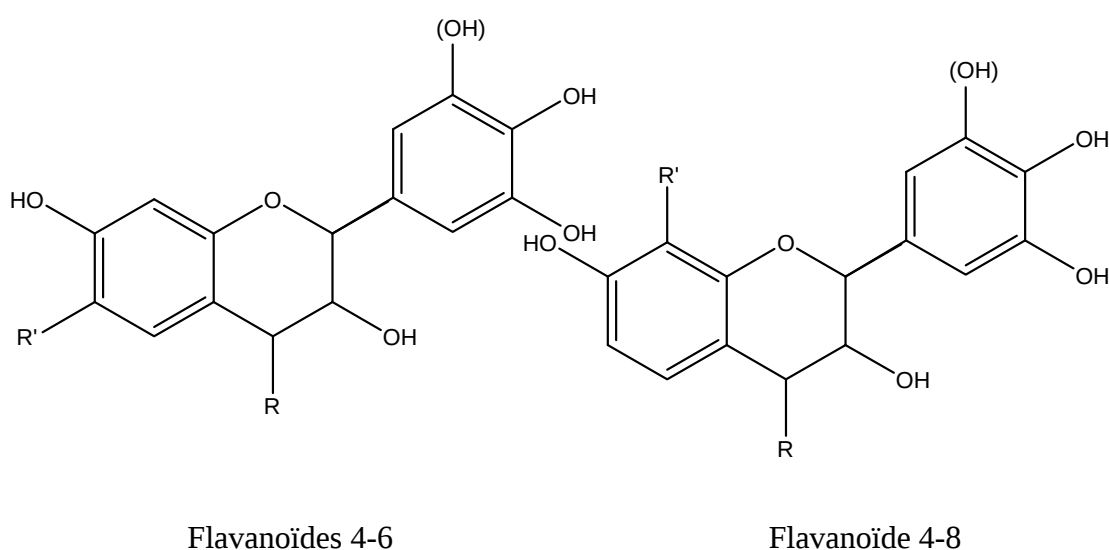


Figure 5 : Structure chimiques des tannins

1.7 Les résines, les substances extractives et le protéines

Ils représentent une faible proportion de la masse totale du bois. Cette proportion varie à la fois entre le feuillus et le résineux et entre les différentes espèces.

Les résines sont des isomères d'acide abiétique, elles sont extraites du bois et peuvent avoir différentes utilisation industrielles (le papier, les pneus...etc.)

Les terpènes comprennent une famille de molécules oligomères de l'isoprène que l'on obtient directement à partir de plusieurs espèces végétales. Les principaux représentants de cette fraction prépondérante sont l' α - pinène et le β - pinène [1].

Les jiomes végétales sont des triglycérides résultant de la condensation de trois molécules d'acides gras avec le glycérol. Elles peuvent être classées en deux familles : les huiles non siccatives et les huiles siccatives. Les principaux acides gras que l'on rencontre sont les acides palmitique, stéarique, oléique, linolénique et éléostéarique [1].

Les substances extractives contiennent une faible quantité de substances phénolique autre que les tannins. Nous citons l'éthyle phénol et l'hydroxylbenzaldéhyde.

Le bois contient, également, une certaine quantité de protéines et de sels de calcium, de magnésium et de potassium [5].

Le grande partie de ces substance est éliminée au cours des différentes étapes de délignification et de blanchiment, mais des analyses ont montré leur présence dans les feuilles de papier. La proportion de ces composés restant dans la pâte et le papier dépend des procédés de cuisson et de blanchiment utilisés [3].

1.8 Phénomènes d'adsorption

1.8.1. Origine des charges dans les fibres cellulosiques

Les groupements ionisables dans les fibres cellulosiques provenant des pâtes chimiques blanchit proviennent essentiellement des fonctions acides carboxyliques portées par les hémicelluloses [6]. En effet, ces fonctions sont essentiellement présentes dans les résidus des acides uroniques : qu'il s'agisse du bois de feuillus ou de résineux, les fonctions acides carboxyliques sont présentes dans l'acide 4-O-méthyle- α -D-glucosyluronique qui est relié à des chaines de xylane dans le cas du feuillus et des chaines d'arabinoxylane dans le cas du résineux. Le reste des fonctions carboxyliques sont présentes dans les substances pectiques de la lamelle mitoyenne [6-10].

Les groupements phénoliques présentes dans la lignine dans les pâtes à haut rendement (TMP, CTMP) sont ionisables dans des conditions alcalines [10]. Les

groupements hydroxyles alcooliques sont considérés comme des acides faibles qui ne sont ionisables qu'en présence de bases fortes.

Le traitement chimique de la pâte dans le procédé de fabrication entraîne, suivant les conditions de cuisson et de blanchiment, un changement de l'accessibilité et du nombre de groupement carboxyliques [3,10] :

- En effet, un traitement sulfite, permet d'avoir des groupements d'acides sulfoniques [6].
- Certains agents de blanchiment (ozone, oxygène, peroxyde d'hydrogène) entraînent une augmentation des groupements carboxyliques par oxydation directe de la cellulose [11].

Par contre, dans la pâte mécanique, les groupements carboxyliques, sont majoritairement des acides uroniques, Ils sont pratiquement les seules fonctions chimiques ionisables à des pH neutre ou légèrement alcalin [10].

1.8.2. Les charges aux interfaces

Généralement, la plupart des substances immergées dans un liquide polaire acquièrent une charge électrique qui agit sur la distribution des ions en solution. La variation du potentiel de surface détermine les énergies d'interaction entre les particules et par voie de conséquence, le niveau de stabilité des suspensions [7,8]. Selon la nature de la substance, il existe différents mécanismes de formation de la charge électrique de surface [8].

- ✓ La dissociation de groupes ioniques à la surface des particules (ex : les groupes
 $\text{-COOH} \Rightarrow \text{-COO}^-$ à la surface des fibres + H_3O^+ dans la solution aqueuse).
- ✓ L'adsorption d'ions de la solution à la surface des particules.
- ✓ L'échange ionique dû à une substitution partielle de certains ions par d'autres de valence différente.

La dissociation et l'adsorption sont les sources les plus communes dans les procédés de fabrication papetiers. Ces mécanismes, et donc les charges de surface, sont grandement affectés par le pH, la conductivité et la température [9].

2.1.1 La double couche électrique

L'interprétation moderne de la double couche électrique montrée sur la figure 1. Elle est divisée en deux couches : couche interne et couche diffuse. La couche interne (encore appelée couche de Sterne) est subdivisée en deux sous couches, la couche interne Helmholtz et la couche externe Helmholtz. Cette couche à une épaisseur de l'ordre de 0,5 μm . La charge de la surface de la particule est équilibrée par une distribution inégale des contre-ions et co-ions dans la solution.

La charge des solides + la charge de la couche interne + la charge de la couche diffuse est elle-même électriquement neutre. L'aspect le plus important de cette double couche est que les ions hors de ce plan de coupe de la couche diffuse sont mobiles en accord avec la particule [8].

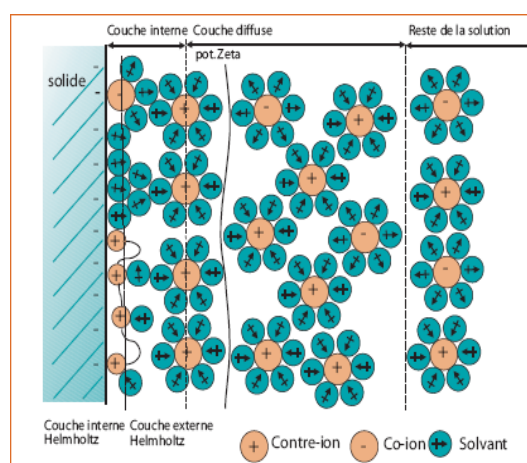


Figure 6 : Structure de la double couche électrique

1.4.4. Les Phénomènes électrocinétiques

Comme on l'a vu, lorsque des particules sont mises en suspension, l'interface (entre le solide et la solution) devient généralement le siège de phénomène électrostatique en raison de l'établissement d'un potentiel de surface. Si l'une des parties de la double couche électrique est en mouvement par rapport à l'autre, des phénomènes électriques sont observés [7].

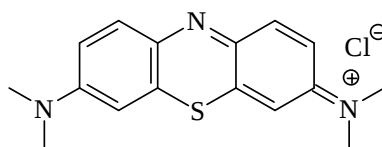
Ces phénomènes dits « électrocinétiques » mettent en évidence le potentiel électrocinétique développé par des particules mises en suspension dans un milieu liquide [6] ; ils peuvent se distinguer suivant l'effet observé et la force ionique du milieu :

- ✓ L'électrophorèse qui désigne le mouvement des particules par rapport au liquide dans une suspension soumise à un champ électrique.
- ✓ le potentiel de sédimentation qui résulte de l'apparition d'un champ électrique dans une suspension soumise à un mouvement (sédimentation, centrifugation,.....).
- ✓ L'électro-osmose qui permet d'observer, sous une différence de potentiel électrique, le mouvement du liquide par rapport à une paroi solide (tube capillaire, membrane....).
- ✓ le potentiel d'écoulement qui résulte de l'écoulement d'un fluide à travers un milieu poreux sous l'effet d'une différence de pression.

1.5. Le bleu de méthylène

Le bleu de méthylène est un composé chimique aromatique hétérocyclique avec la formule chimique brute suivante : $C_{16}H_{18}ClN_3S$. D'après la nomenclature IUPAC, le nom du composé chimique correspondant au bleu de méthylène est le : chlorure de bis-(diméthylamino)- 3,7 phenazathionium. A température ambiante le bleu de méthylène est une poudre fine, inodore et de couleur verte foncée. La structure chimique de ce colorant est montrée dans formule 16 [11-15].

Ce colorant est utilisé en biologie ou en chimie. De plus, le bleu de méthylène est employé couramment comme indicateur redox en chimie analytique. Sa présence dans des solutions aqueuses donne des colorations bleues dans un environnement oxydant, mais deviennent incolores quand elles sont exposées à un agent réducteur. Les solutions aqueuses du bleu de méthylène absorbent à des longueurs d'onde maximales de 665 nanomètres. Cette propriété est exploitée, car elle est particulièrement intéressante en raison de sa simplicité [14]. Un grand nombre d'expérience utilisant ce colorant pour des études de la cinétique d'adsorption des matériaux fibreux comme la sépiolite par exemple [15].



(16)

2. PARTIE EXPERIMENTALE

2.1. Suspensions de pâtes

Trois différentes pâtes ont été utilisées comme matière première, notamment:

- ✓ Pâte kraft blanchie à partir de feuillu (Eucalyptus), et notée “HW”.
- ✓ Pâte kraft blanchie à partir de résineux (mélanges de pins et d’épicéa, fournies par l’usine de Tarascon) et désignée “SW”.
- ✓ Linters de coton, “CL”.

✓ 30 g de pâtes sèches ont été mélange avec de l’eau desionisée pendant 16 heures. Ensuite, la suspension de pâte a été désintégrée en utilisant un mixeur classiquement utilise a cet effet et nommé (Lhomergy). Cette opération a été fait 500

tour et avait pour but l'individualisation des fibres. Cette suspension sera nommée "pâte non raffinée" tout le long du présent manuscrit. Toutes les suspensions fibreuses ont été raffinées à trois niveaux : 3000, 6000 et 10000 rotations, respectivement.

La consistance de toutes les suspensions de pâtes étudiées était de 1g/L (dans la solution de 0,6 mM barbital comme solution tampon et dans l'eau deionisée si le cas non tampon par rapport à la fibre sèche). Une solution tampon (voir plus loin) a été additionnée pour maintenir un pH constant durant les expériences d'adsorption de bleu de méthylène.

On utilisera les abréviations suivantes pour designer toutes les suspensions étudiées dans cette thèse :

HW-0, HW-3000, HW-600, HW-10000, pour la pâte kraft blanchies (Eucalyptus), raffinée à 0, 3000, 6000 et 10000 rotations, respectivement.

SW-0, SW-3000, SW-600, SW-10000, pour la pâte kraft blanchies (résineux), raffinée à 0, 3000, 6000 et 10000 rotations, respectivement.

CL-0, CL-3000, CL-600, CL-10000, pour la pâte de linters de coton, raffinée à 0, 3000, 6000 et 10000 rotations, respectivement.

2.3. Préparation des solutions

Les différentes solutions ont été préparées :

1. NaOH 2M a été préparé par peser quantité de NaOH dans l'eau deionisée.
2. Tampon 0,6 mM dans 0,4 mM NaOH barbital a été préparé par dilué de solution de barbital 0,06 M dans NaOH 0,04 M.
3. Bleu de méthylène $3,82 \times 10^{-4}$ M dans barbital 0,6 mM a été préparé par dilué une quantité précise de bleu de méthylène sèche dans barbital 0,6 mM.

4. Bleu de méthylène $7,63 \times 10^{-3}$ M (20C) dans barbital 0,6 mM a obtenu par dilué un quantité exactement de bleu de méthylène sèche dans barbital 0.6 mM.

5. Solution bleu de méthylène aux différentes concentration de 2C, 5C, 7C, 10C et 15C a obtenu par dilué de solution de bleu méthylène $7,63 \times 10^{-3}$ M dans barbital 0,6 mM.

6. Solution de poly(DADMAC) 0,1% (w/w) a été préparé en diluant un quantité de poly(DADMAC) dans l'eau desionisée.

7. Solution NaCl 0,1 M été préparé par précisé de quantité de NaCl dans l'eau desionisée.

2.4. Courbes de calibration et isothermes d'adsorption

Les courbes de calibration ont été construites en mesurant plusieurs concentrations de solutions bleu de méthylène (BM) diluée dans la solution barbital 0,6 mM que nous avons appliqué de l'autre, [16,17].

2.5. Isothermes d'adsorption par spectroscopie d' UV-Visible

Pour les isothermes d'adsorption, 500 ml de suspension des fibre (préparé comme partie 2.1) dans eau desionisée ou de solution tampon (ça dépende de cas) ont été préparé et maintenu sous agitation. Ensuite, des solutions des quantités croissantes de BM ont été ajouté à la suspension fibreuse maintenu sous agitation et tamponné à un pH de 7,8. Le temps de réaction a été varié entre 2 minutes et 16 heures pour le cas eau desionisée et ont montré que l'adsorption était rapide (les premières minutes). Un temps d'adsorption entre 5 et 30 minutes a été choisi pour toutes expériences. A la fin de la réaction, le mélange à été filtré deux fois à travers un filtre en verre fritté n°2 (40-100 μm de taille de pores) et le filtrat à été analysé par un spectrophotomètre UV visible à la longueur d'onde d'adsorption maximale du BM, c'est-à-dire à 664 nm. Dans tous les cas, une solution référence obtenue par une double filtration de la suspension fibreuse et en absence du BM a été utilisée. Toutes les expériences impliquant l'adsorption du BM ont été menées dans une vaisselle métallique, quand

c'est possible. Dans les cas où cela était impossible, la vaisselle en verre a été totalement recouverte de papier en aluminium.

La quantité de BM adsorbée a été calculée par différence entre la quantité de BM introduit dans le milieu réactionnel et celle mesurée dans le filtrat à la fin de l'adsorption.

2.6. Potentiel zêta

L'appareil utilisé pour les mesures est appelé SZP-04 (système zêta potentiel). Un échantillon de suspension fibreuse 1% est filtré pour former un matelas de fibres sur l'électrode grille. Lorsque le matelas fibreux est compact, une pompe à vide est mise en route pour faire varier la pression entre -0,2 et -0,4 bar d'une manière alternative. Sous l'effet de la différence de pression, une circulation d'eau s'établit et entraîne le déplacement des contre-ions du matelas fibreux, ce qui permet la création d'un potentiel d'écoulement entre l'électrode grille et l'électrode anneau (voir figure 7).

La valeur du potentiel zêta est déterminée en mesurant les paramètres suivants :

- Potentiel d'écoulement.
- Conductivité.
- Différence de pression.

La valeur du potentiel zêta est calculée par la formule de Helmholtz-Smoluchowski suivante :

$$\zeta = \frac{4\pi\eta U\chi G}{\varepsilon\Delta P} \dots\dots\dots 1$$

Où :

η : Viscosité de l'eau (1mPa.s à 20°C).

ε : Constante diélectrique (F/m) (80,20 à 20°C, [33].

χ : Conductivité électrique de la suspension fibreuse (S/m).

U : Potentiel d'écoulement (mV).

Δp : Différence de pression (Pa).

ζ : Potentiel zêta (mV).

G : Constante appareil.

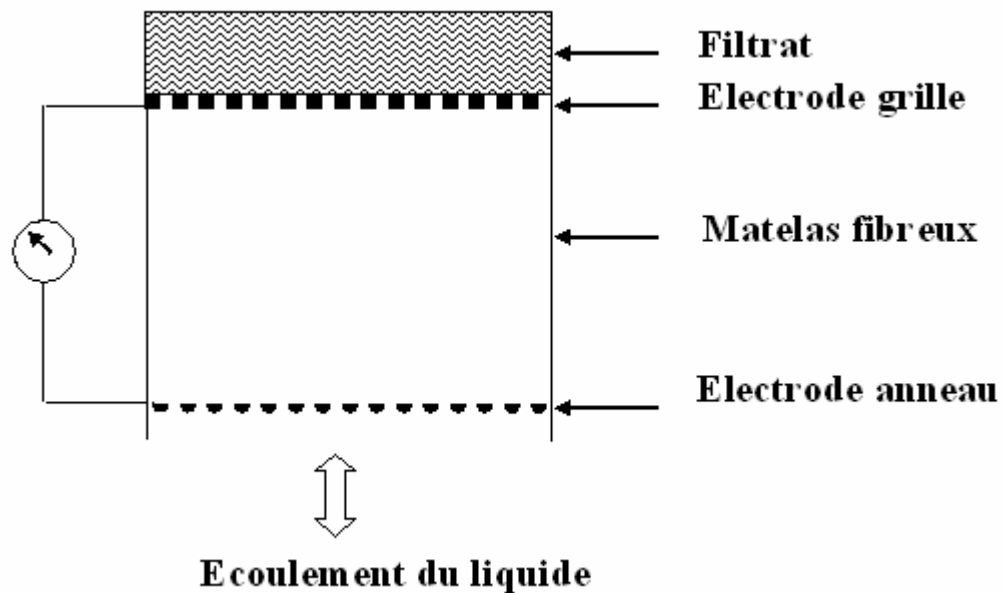


Figure 2. Principe de fonctionnement de l'appareil de mesure du potentiel zêta (SZP04), utilisé dans ce travail.

Une étude effectuée au niveau du LGP2 [18] a révélé que cet appareil ne dispose pas d'un dispositif de mesure de la température et a supposé que l'expérience se déroulait à une température de 20°C et à une viscosité de l'eau de 1 mPa.s. Aussi cet appareil mesure la conductivité électrique dans le matelas fibreux formé qui est différente de celle de la suspension fibreuse ce qui influe sur la valeur calculée du potentiel zêta, conséquence, toutes les valeurs de potentiel zêta mesurées par la méthode du potentiel d'écoulement présentait dans sont travail ont été corrigées en tenant compte des valeurs réelles de la viscosité de l'eau (à la température de la mesure) et de la conductivité de la suspension fibreuse [18].

$$\zeta_{real} = \frac{\eta_{real} \chi_{real}}{0,001 \chi_{ap}} \zeta_{ap} \dots\dots\dots 2$$

Avec :

$\zeta_{réel}$: Valeur réelle du potentiel zêta

ζ_{ap} : Valeur du potentiel zêta mesurée par le SZP-04.

$\eta_{réel}$: Viscosité de l'eau à la température de mesure.

$\chi_{réel}$: Valeur de la conductivité mesurée par un conductimètre *JENWAY 4330*.

χ_{ap} : Valeur de la conductivité mesurée par le SZP-04.

Dans notre travail on s'intéresse qu'aux valeurs du potentiel zêta mesurées par le SZP-04.

3. PARTIE RESULTATS ET DISCUSSIONS

3.1 Sorption de bleu méthylène sur cellulose avec non raffiné et raffiné des pâtes aux 3 niveaux différents à température ambiante

Premierements, nous avons cherché longueur d'onde d'adsorption maximale de bleu méthylène. Nous avons essayé de préparé plusieurs solution de bleu méthylène aux différent de concentrations. On a trouvé que l'absorbance maximale présence à longueur d'onde à 664 nm. pour spectroscopie de UV-Visible. Les spectres deVisible de bleu méthylène à montre comme dans la figure 8.

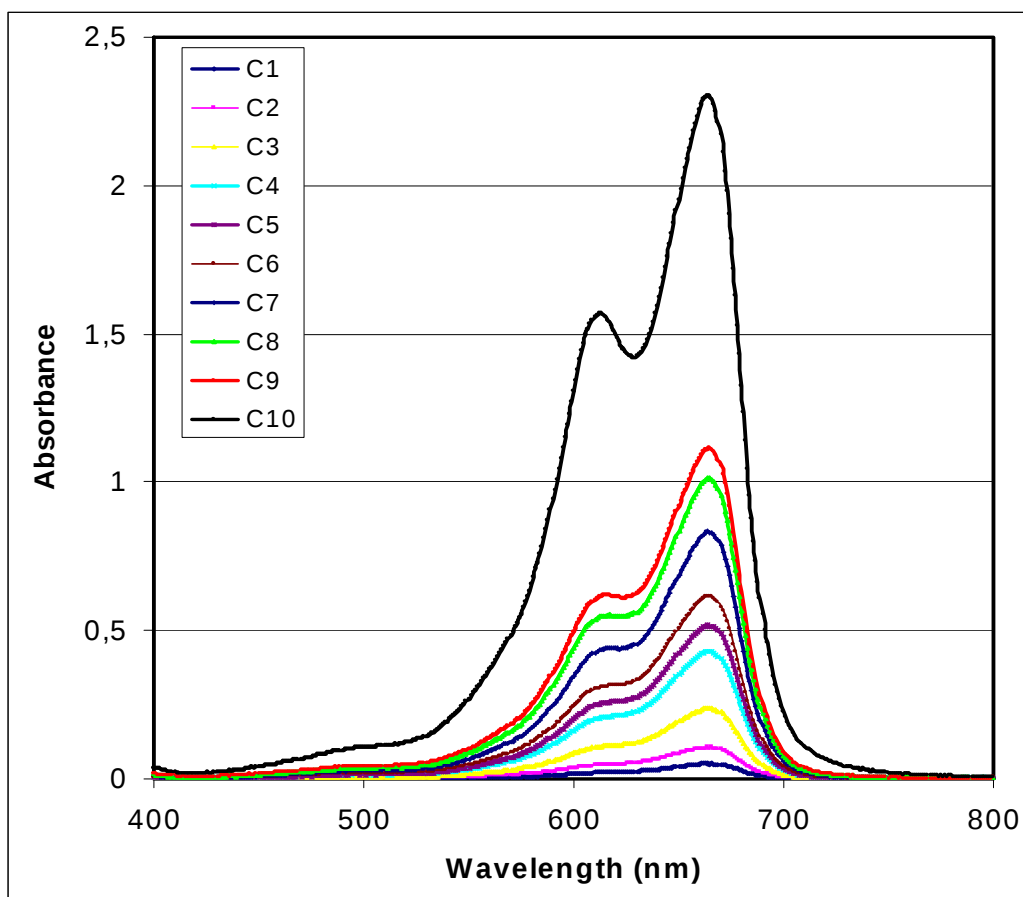


Figure 8 : Spectre Visible de bleu méthylène

3.2 Courbe de calibration de bleu méthylène

La Figure 9 et Tableau 1 montre la courbe de calibration établie pour déterminer sorption de bleu méthylène. On peut déduire que la linéarité entre l'adsorption des solutions du BM et leur concentration.

Tableau 1 : Absorbance de bleu méthylène pour le courbe de calibration

Concentration de bleu méthylène ($\mu\text{mol/L}$)	Absorbance
0,00	0,00
1,53	0,11
3,05	0,24
7,63	0,58
15,26	1,13

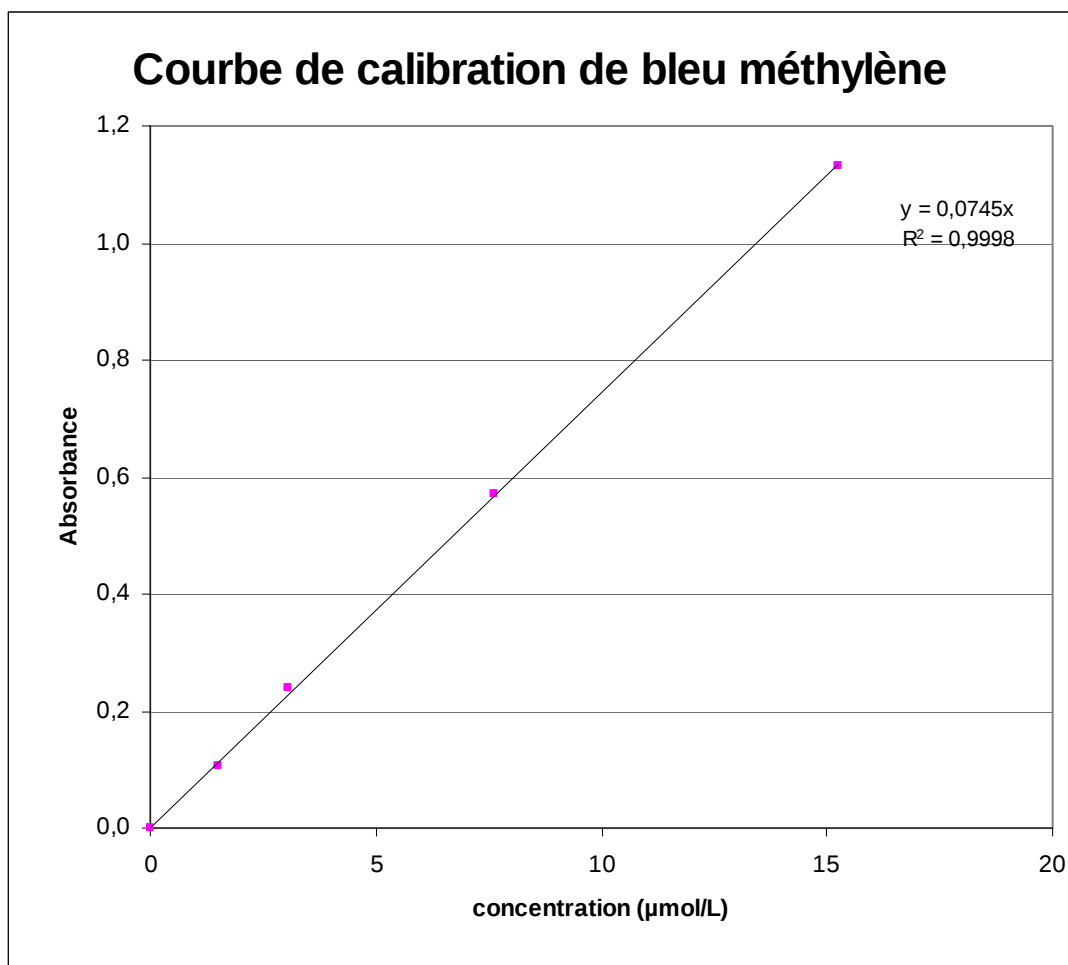


Figure 9 : Courbe de calibration de bleu méthylène

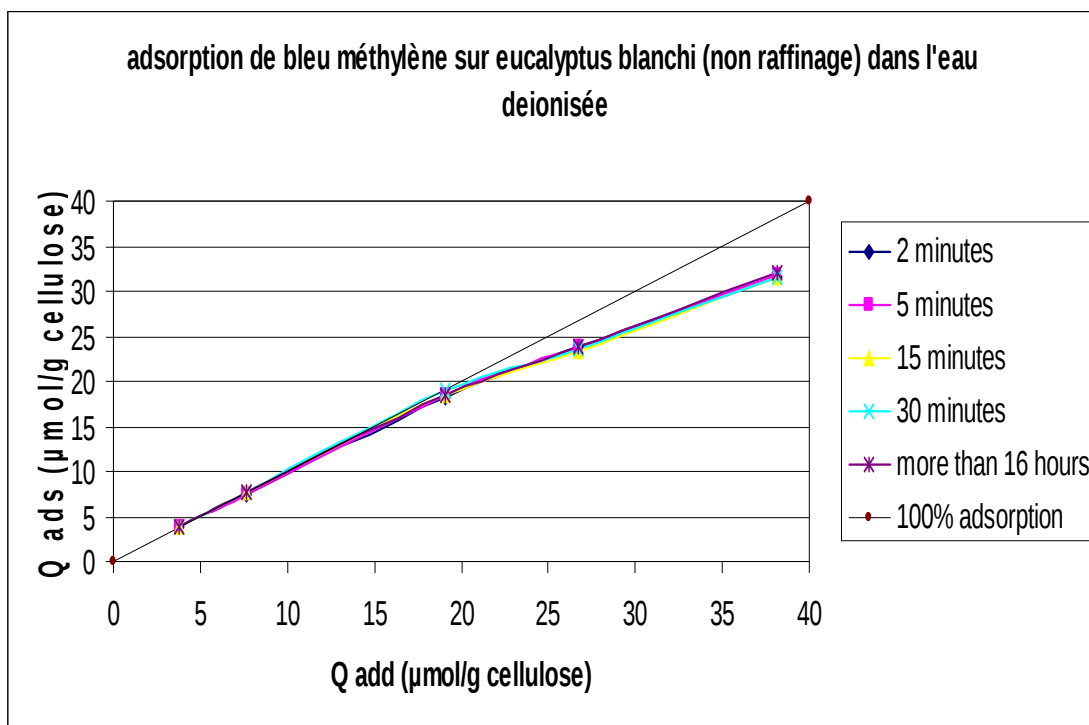


Figure 10 : Adsorption de bleu méthylène sur eucalyptus blanchi (non raffinage) dans l'eau desionisée.

On a essayé de faire expérience sur adsorption de bleu méthylène dans suspension d'eucalyptus blanchi (non raffinage) dans l'eau desionisée. On a trouvé que la réaction été complété dans 2 minutes. Cet adsorption d'isotherme a montré dans la Figure 10.

Tableau 2 : Adsorption de bleu de méthylène sur eucalyptus blanchi dans l'eau desionisée pendant 30 minutes

Type de pâte	Concentration de bleu méthylène (M)	Q add ($\mu\text{mol/g}$ cellulose)	Q ads ($\mu\text{mol/g}$ cellulose)	% adsorption
Eucalyptus blanchi (non raffinage)	C	3,82	3,78	99,18
	2C	7,63	7,20	94,35
	5C	19,08	17,47	91,58
	7C	26,71	23,76	88,95
	10C	38,16	33,31	87,30
Eucalyptus blanchi (PFI 3000)	C	3,82	3,89	101,84
	2C	7,63	7,21	94,42
	5C	19,08	15,72	82,39
	7C	26,71	20,72	77,57
	10C	38,16	27,98	73,31
Eucalyptus blanchi (PFI 6000)	C	3,82	3,78	99,18
	2C	7,63	7,20	94,35
	5C	19,08	17,47	91,58
	7C	26,71	23,76	88,95
	10C	38,16	33,31	87,30
Eucalyptus blanchi (PFI 10000)	C	3,82	3,73	97,85
	2C	7,63	7,11	93,11
	5C	19,08	17,96	94,15
	7C	26,71	23,00	86,09
	10C	38,16	27,68	72,54

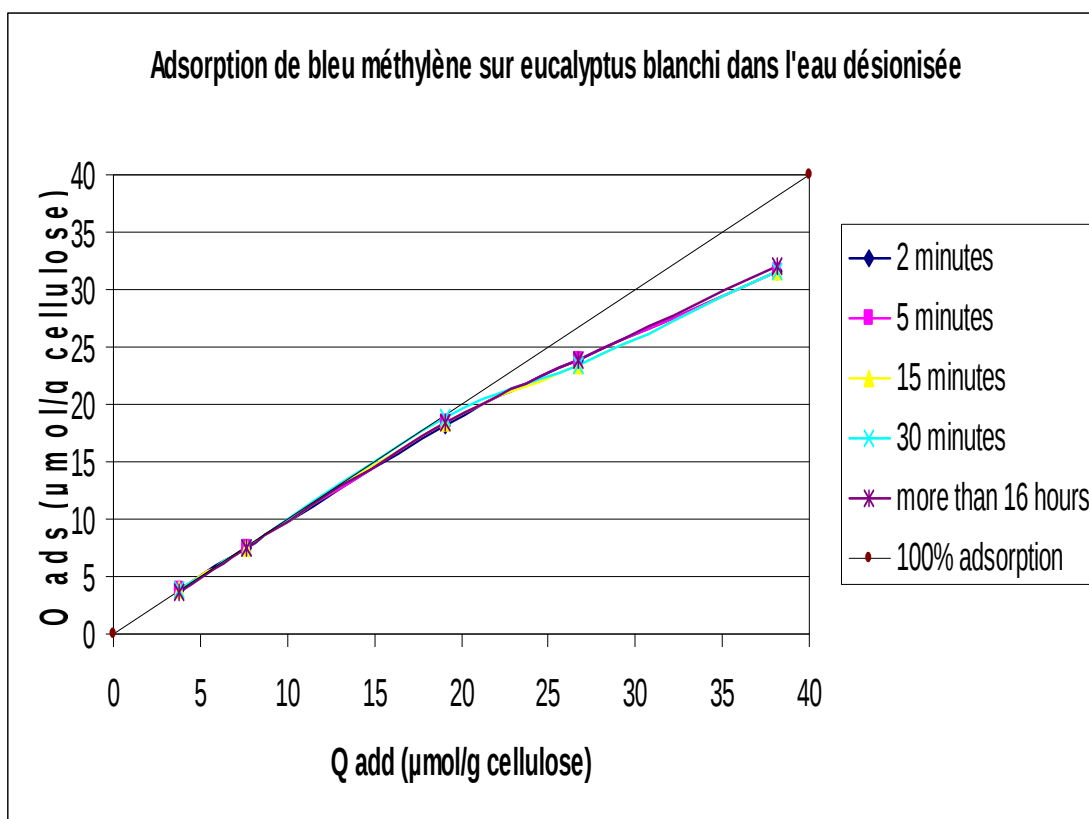


Figure 11 : Comparision d'adsorption de bleu de méthylène sur eucalyptus blanchi aux 3 niveaux de raffinage : 30 minutes

Comparasion d'adsorption d'eucalyptus blanchi (non raffinage) et raffinage aux niveaux de PFI 3000, 6000 and 10000 sont montré dans la Figure 11 et le data est dans le tableau 2.

Eucalyptus blanchi

Tableau 3 : Sorption de bleu de méthylène sur eucalyptus blanchi (non raffinage et raffinage) pendant 30 minutes.

Type de pâte	Concentration de bleu méthylène (M)	Q add ($\mu\text{mol/g}$ cellulose)	Q ads ($\mu\text{mol/g}$ cellulose)	% adsorption
Eucalyptus blanchi (non raffinage)	2C	7,64	7,45	97,53
	5C	19,09	18,90	98,98
	7C	26,71	26,32	98,54
	10C	38,15	34,79	91,19
	15C	57,23	41,74	72,92
	20C	76,31	45,84	60,07
Eucalyptus blanchi (PFI 3000)	2C	7,63	7,44	97,42
	5C	19,08	15,62	81,88
	7C	26,71	19,94	74,64
	10C	38,16	21,70	56,87
	15C	57,23	27,72	48,44
	20C	76,31	23,40	30,67
Eucalyptus blanchi (PFI 6000)	2C	7,64	6,81	89,11
	5C	19,10	15,68	82,09
	7C	26,71	19,94	74,64
	10C	38,20	31,85	83,38
	15C	57,23	1,62	2,83
	20C	76,31	-2,53	-3,31
Eucalyptus blanchi (PFI 10000)	2C	7,64	7,46	97,69
	5C	19,10	17,31	90,65
	7C	26,71	26,39	98,82
	10C	38,15	35,97	94,28
	15C	57,23	40,99	71,63
	20C	76,31	47,94	62,82

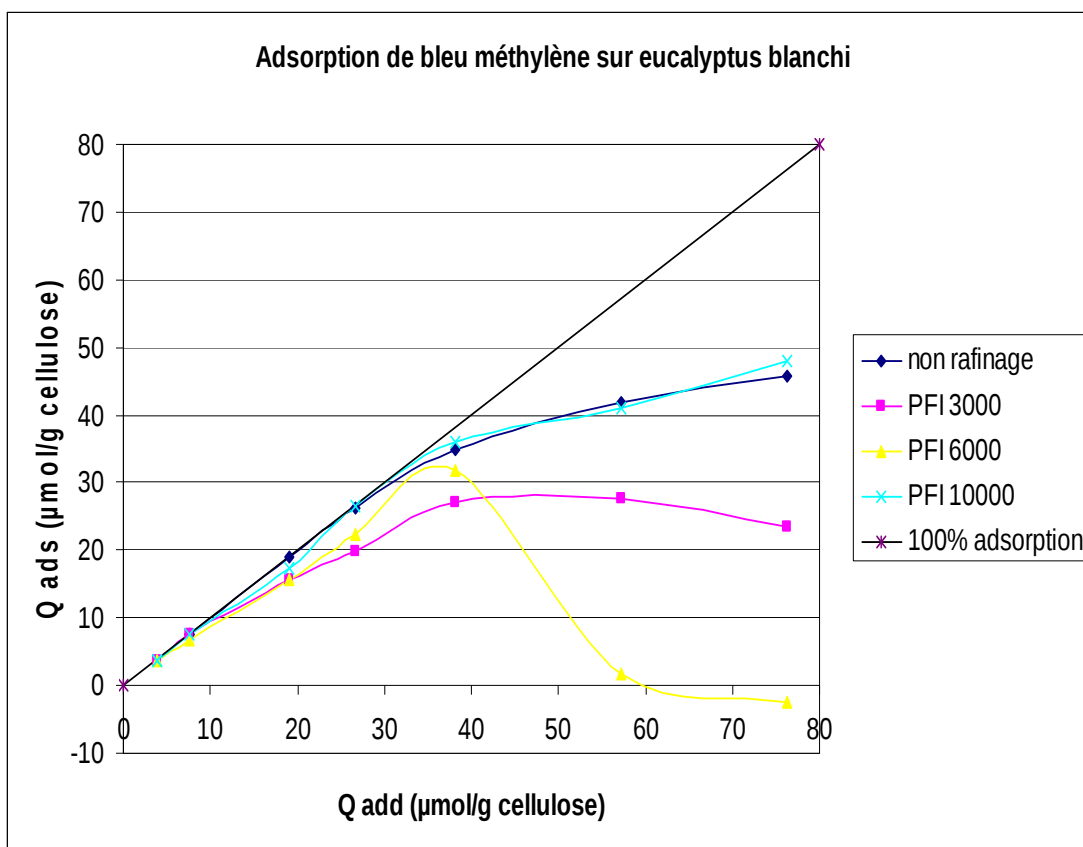


Figure 12 : Comparision d'adsorption de bleu de méthylène sur eucalyptus blanchie aux 3 niveaux de raffinage : 30 minutes

On a changé de media dans la suspension des fibres. On a choisi solution 0,6 mM barbital pour contrôle le pH. Adsorption d'isotherme de bleu méthylène sur eucalyptus blanchi, (non raffinage et raffinage à ces trois niveaux) sont dans la Figure 12 et 14, relativement. Ceux de résineux de Tarascon (raffinage à trois niveaux) sont montrés dans la Figure 13.

Résineux de Tarascon

Tableau 4 : Sorption de bleu de méthylène sur résineux de Tarascon aux niveaux différents de pâte pendant 30 minutes.

Type de pâte	Concentration de bleu méthylène (M)	Q add ($\mu\text{mol/g}$ cellulose)	Q ads ($\mu\text{mol/g}$ cellulose)	% adsorption
Résineux de Tarascon (PFI 3000)	2C	7,63	7,45	97,62
	5C	19,08	16,48	86,36
	7C	26,71	22,36	83,72
	10C	38,16	24,02	62,94
	15C	57,24	26,42	46,16
	20C	76,32	21,05	27,59
Résineux de Tarascon (PFI 6000)	2C	7,63	7,65	100,21
	5C	19,08	15,13	79,32
	7C	26,71	25,32	94,77
	10C	38,16	20,22	52,98
	15C	57,24	26,42	46,16
	20C	76,32	22,36	29,30
Résineux de Tarascon (PFI 10000)	2C	7,63	5,82	76,23
	5C	19,08	13,89	72,82
	7C	26,71	17,54	65,68
	10C	38,16	21,70	56,87
	15C	57,24	27,12	47,38
	20C	76,32	25,86	33,88

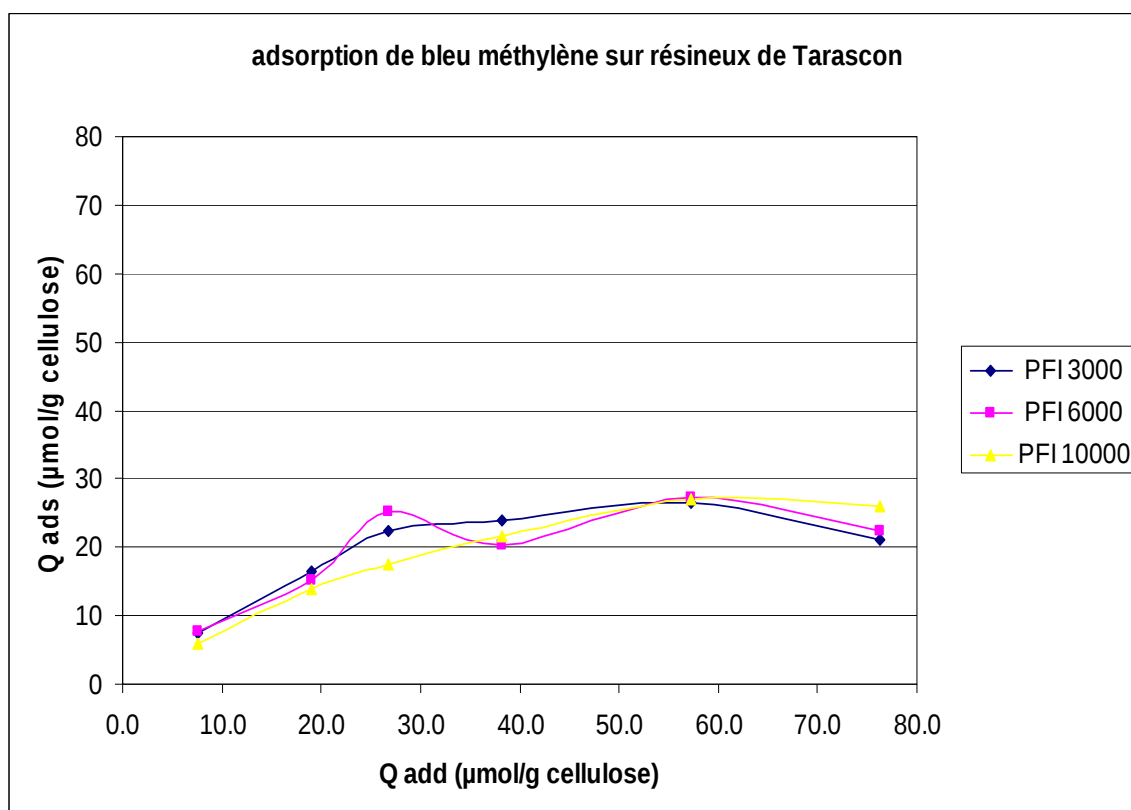


Figure 13 : Comparision d' adsorption de bleu de méthylène sur résineux de Tarascon aux trois niveaux de raffinage : 30 minutes

Cotton linter

Tableau 5 : Sorption de bleu méthylène sur non raffinage et raffinage de linter cotton pendants 30 minutes.

Type de pâte	Concentration de bleu méthylène (M)	Q add ($\mu\text{mol/g}$ cellulose)	Q ads ($\mu\text{mol/g}$ cellulose)	% adsorption
Cotton Linter (non raffinage)	2C	7,63	4,14	54,24
	5C	19,08	3,55	18,63
	7C	26,71	4,75	17,79
	10C	38,15	5,85	15,34
	15C	38,15	5,85	15,34
	20C	76,31	3,76	4,92
Cotton linter (PFI 3000)	2C	7,63	3,93	51,50
	5C	19,08	4,94	25,88
	7C	26,72	4,23	15,85
	10C	38,16	6,17	16,16
	15C	57,25	0,06	7,27
	20C	76,36	5,82	7,62
Cotton linter (PFI 6000)	2C	7,63	4,25	55,63
	5C	19,08	6,34	33,21
	7C	26,72	4,90	18,31
	10C	38,18	7,49	19,62
	15C	57,25	5,39	9,42
	20C	76,36	11,75	15,39
Cotton linter (PFI 10000)	2C	7,63	4,26	55,85
	5C	19,08	3,66	19,19
	7C	26,72	4,24	15,86
	10C	38,16	2,93	7,68
	15C	57,26	2,25	3,93
	20C	76,32	16,60	25,86

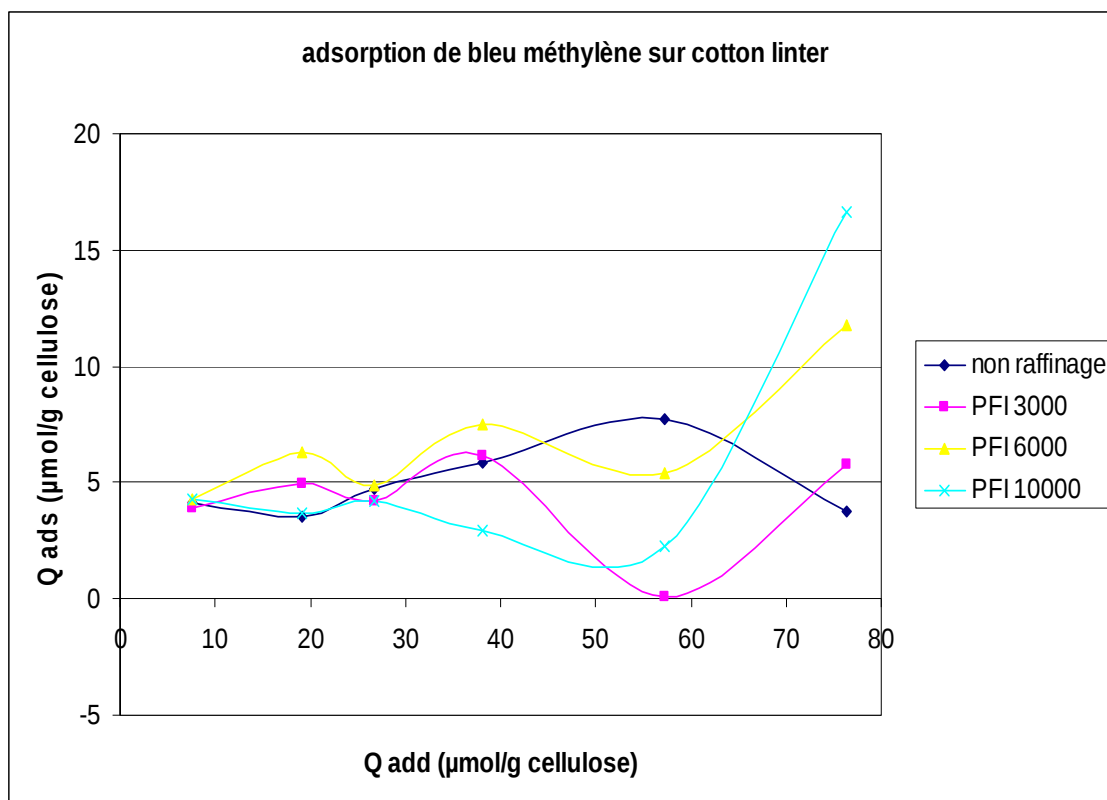


Figure 14 : Comparision d' adsorption de bleu de méthylène sur cotton linter aux 3 niveaux de raffinage : 30 minutes

On ne peut pas dit plus sur adsorption de bleu méthylène sur les suspensions de fibres. On pensiez qu'il y un désorption de réaction.

Quand on comparé l'adsorption d'isotherme de résineux de Tarascon et cotton linter. On a trouvé que l'adsorption de résineux de Tarascon (raffinage à trois niveaux) ne sont pas trop déférent quand on comparé ceux de cotton linter, la raison peut être considéré comme la nature de pâte, la taille du pore, volume du pore, mais il faut mieux de faire dans le future les autre expériences qu'on a pas faire.

3.3 Potentiel Zêta

Pour mieux comprendre sur adsorption de fibre, nous avons étudié la méthode potentiel zêta avec poly(DADMAC) comme polyélectrolyte.

3.3.1. Pâtes initial

On peut déterminer demande cationique dans les pâtes. Cette valeur montre de quantité de group anionique qui reflète le group carboxyl dans la pâte. Les résultats de potentiel zêta à trois niveaux de raffinage de pâte sont montrés dans le tableau 6.

Tableau 6 : Potentiel Zêta de pâtes raffinage aux 3 niveaux différentes

Niveaux de raffinage	Potential Zêta (mV)		
	Eucalyptus blanchi	Resineux de Tarascon	Cotton linter
0	-27,60	-17,3	-20,6
3000	-27,40	-17,9	-18,5
6000	-24,20	-17,6	-16,8
10000	-24,20	-17,7	-14,8

3.3.2. Evolution de potentiel zêta d'addition de poly(DADMAC)

3.3.2.1. Eucalyptus blanchi

Demande cationique de pâte eucalyptus blanchi, résineux de Tarascon et cottonlinter à trois niveaux de raffinage a montré dans le tableau 7, 12 et 18 pour la pâte eucalyptus blanchi, résineux de Tarascon et cotton linter, respectivement.

Tableau 7 : Demande cationique de eucalyptus blanchi aux 3 niveaux de raffinage

Eucalyptus blanchi	poly(DADMAC) (% massique)	Demande cationique ($\mu\text{eq/g}$ de cellulose)
Non raffinage	0,036	2,2
PFI 3000	0,12	7,4
PFI 6000	0,19	11,8
PFI 10000	0.275	17,0

Tableau 8 : Potentiel Zêta de quantité Poly(DADMAC) sur eucalyptus blanch non raffinage)

Taux de Poly(DADMAC)		Résultats	
concentration (%)	V ajoutée (ml)	Potentiel Zêta (mV)	Conductivité (mS)
0	0	-27.60	0.523
0,05	0,5	-19,90	0,517
0,10	1,0	-8,80	0,477
0,15	1,5	-2,80	0,510
0,20	2,0	4,40	0,539
0,25	2,5	7,10	0,516
0,30	3,0	14,20	0,530

Tableau 9 : Potentiel Zêta de quantité Poly(DADMAC) sur eucalyptus blanchi PFI 3000

Taux de Poly(DADMAC)		Résultats	
concentration (%)	V ajoutée (ml)	Potentiel Zêta (mV)	Conductivité (mS)
0	0	-27,60	0,523
0,01	0,5	-19,90	0,517
0,02	1,0	-8,80	0,477
0,03	1,5	-2,80	0,510
0,04	2,0	4,40	0,539
0,05	2,5	7,10	0,516
0,06	3,0	14,20	0,530

Tableau 10 : Potentiel Zêta de quantité de Poly(DADMAC) sur eucalyptus blanchi PFI 6000

Taux de Poly(DADMAC)		Résultats	
concentration (%)	V ajoutée (ml)	Potentiel Zêta (mV)	Conductivité (mS)
0,00	0,0	-24,20	0,609
0,06	3,0	-18,90	0,393
0,10	5,0	-13,40	0,621
0,14	7,0	-7,30	0,556
0,16	8,0	-3,90	0,515
0,18	9,0	-2,50	0,511
0,20	10,0	1,60	0,600

Tableau 11 : Potentiel Zêta de quantité de Poly(DADMAC) sur eucalyptus blanchi PFI 10000

Taux Poly(DADMAC)		Résultats	
concentration (%)	V ajoutée (ml)	Potentiel Zêta (mV)	Conductivité (mS)
0,00	0	-24,20	0,548
0,10	5	-17,40	0,545
0,16	8	-10,90	0,544
0,20	10	-7,30	0,54
0,24	12	-3,30	0,539
0,30	15	1,90	0,558
0,34	17	4,30	0,526

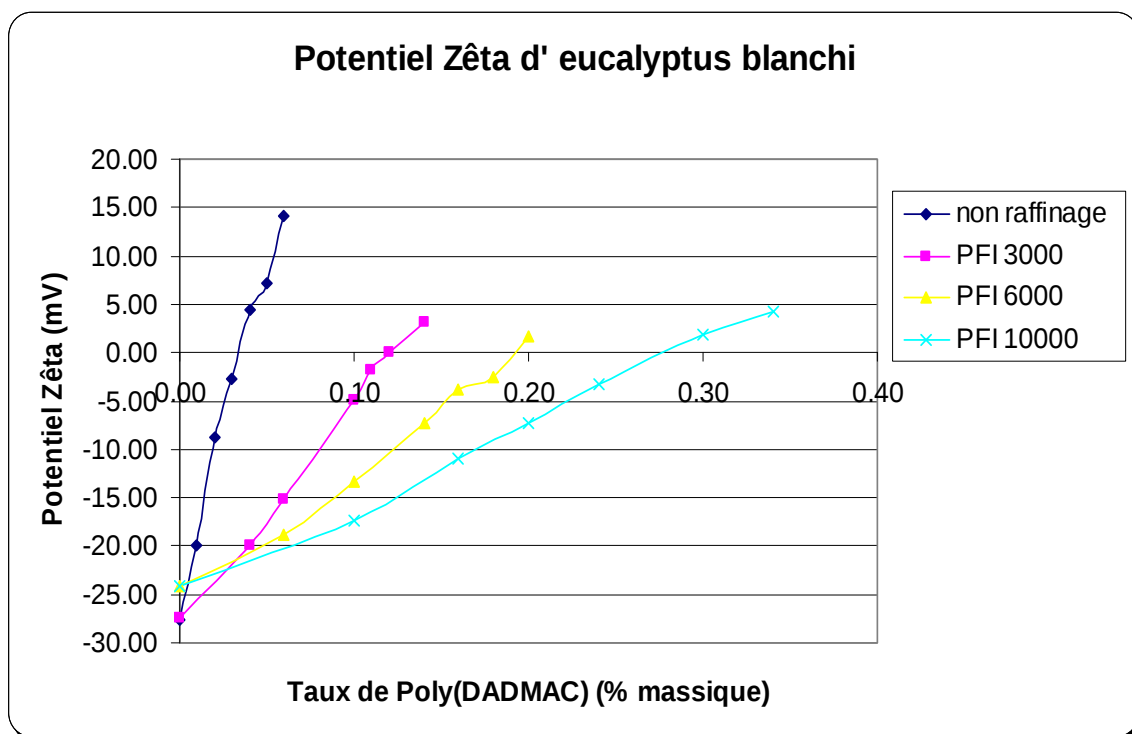


Figure 15 : Comparision de potential zêta d'eucalyptus blanchi.

Potentiel zêta d'eucalyptus blanchi (non raffinage et raffinage) quand on a ajoutée poly(DADMAC) dans les suspensions de fibres a montré dans la Figure 15. Ceux pour résineux de Tarascon et cotton linter ont montré dans les Figure 16 et 17, respectivement.

3.3.2.2. Softwood of Tarascon

Tableau 12 : Cationique demande de résineux de Tarascon aux 3 niveaux raffinage.

Résineux de Tarascon	poly(DADMAC) (% massique)	Demande cationique ($\mu\text{eq/g}$ de cellulose)
Non raffinage	0,02	0,6
PFI 3000	0,06	3,7
PFI 6000	0,08	4,9
PFI 10000	0,12	7,4

Tableau 13 : Potentiel Zêta de quantité Poly(DADMAC) sur résineux de Tarascon

Taux Poly(DADMAC)		Résultats	
concentration (%)	V ajoutée (ml)	Potentiel Zêta (mV)	Conductivité (mS)
0,00	0	-17,30	0,430
0,00	0,2	-9,70	0,425
0,01	0,4	-2,90	0,427
0,01	0,6	1,00	0,427
0,02	1,0	3,60	0,425
0,04	2,0	22,10	0,439
0,06	3,0	39,60	0,431

Tableau 14 : Zeta potentiel de quantité de Poly(DADMAC) sur résineux de Tarascon PFI 3000

Taux de Poly(DADMAC)		Résultats	
concentration (%)	V ajoutée (ml)	Potentiel Zêta (mV)	Conductivité (mS)
0,00	0	-17,90	0,614
0,01	0,5	-10,60	0,620
0,02	1,2	-7,30	0,630
0,03	1,7	-4,90	0,640
0,05	2,3	-2,50	0,660
0,06	3,0	0,00	0,650
0,07	3,6	1,80	0,650

Tableau 15 : Potentiel Zêta de quantité Poly(DADMAC) sur résineux de Tarascon PFI 6000

Taux de Poly(DADMAC)		Résultats	
concentration (%)	V ajoutée (ml)	Potentiel Zêta (mV)	Conductivité (mS)
0,00	0	-17,60	0,535
0,01	0,5	-14,20	0,535
0,03	1,7	-9,60	0,546
0,05	2,3	-6,70	0,538
0,07	3,6	-3,70	0,543
0,08	4,1	1,30	0,202
0,09	4,6	2,80	0,166

Tableau 16 : Potentiel Zêta de quantité de Poly(DADMAC) sur résineux de Tarascon PFI 10000

Taux de Poly(DADMAC)		Résultats	
concentration (%)	V ajoutée (ml)	Potentiel Zêta (mV)	Conductivité (mS)
0,00	0	-17,70	0.565
0,01	0,5	-15,00	0,571
0,03	1,7	-11,50	0,597
0,06	3,0	-7,80	0,591
0,07	3,6	-6,00	0,606
0,09	4,6	-3,60	0,554
0,11	5,6	-1,30	0,554
0,12	6,0	0	0,604
0,13	6,6	0	0,601
0,14	7,0	0,9	0,559

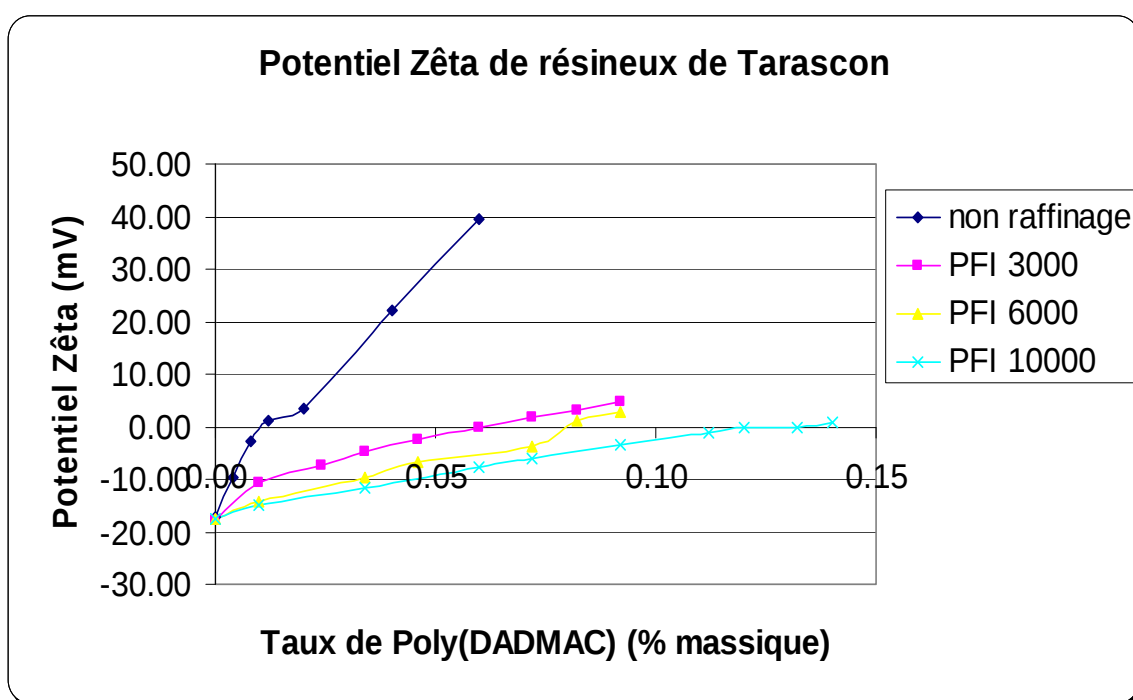


Figure 16 : Comparision de potentiel zêta de résineux de Tarascon aux 3 niveaux de raffinage

3.3.2.3. *Cotton linter***Tableau 17 : Potentiel Zêta de quantité de Poly(DADMAC) sur cotton linter (non raffinage)**

Taux de Poly(DADMAC)		Résultats	
concentration (%)	V ajoutée (ml)	Potentiel Zêta (mV)	Conductivité (mS)
0,00	0	-20,60	0,468
0,00	0,2	-15,20	0,501
0,01	0,4	-10,20	0,466
0,02	0,8	-6,90	0,462
0,02	1,0	-1,20	0,453
0,02	1,2	1,10	0,458
0,03	1,5	8,60	0,462

Tableau 18 : Potentiel Zêta de quantité de Poly(DADMAC) sur cotton linter PFI 3000

Taux de Poly(DADMAC)		Résultats	
concentration (%)	V ajoutée (ml)	Potentiel Zêta (mV)	Conductivité (mS)
0,00	0	-18,50	0,480
0,01	0,5	-11,60	0,483
0,02	0,8	-7,50	0,494
0,02	1,0	-3,60	0,485
0,02	1,2	0,00	0,496
0,03	1,5	5,80	0,498
0,00	0,0	-18,50	0,480

Tableau 19 : Potentiel de quantité d' ajoutée de Poly(DADMAC) sur coton linter PFI 6000

Taux de Poly(DADMAC)		Résultats	
concentration (%)	V ajoutée (ml)	Potentiel Zêta (mV)	Conductivité (mS)
0,00	0	-16,80	0,532
0,01	0,5	-11,00	0,558
0,02	1,0	-3,80	0,510
0,03	1,5	1,90	0,520
0,04	2,0	7,70	0,529
0,05	2,5	12,90	0,534
0,06	3,0	18,20	0,553

Tableau 20 : Potentiel Zêta de quantité Poly(DADMAC) sur coton linter PFI 10000

Taux de Poly(DADMAC)		Résultats	
concentration (%)	V ajoutée (ml)	Potentiel Zêta (mV)	Conductivité (mS)
0,00	0	-14,80	0,519
0,01	0,5	-10,40	0,529
0,02	1,0	-5,80	0,517
0,03	1,5	1,20	0,537
0,04	2,0	4,00	0,518
0,05	2,5	9,40	0,531
0,06	3,0	15,30	0,543

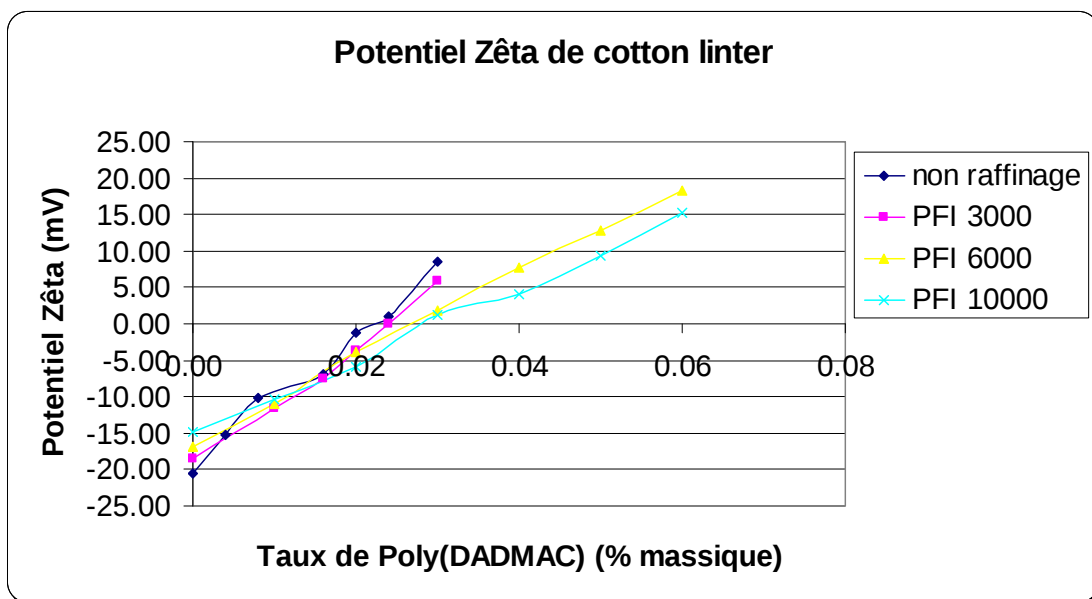


Figure 17 : Potentiel Zêta de linter cotton PFI 10000

Tableau 21 : Demande cationique de cotton linter aux 3 niveaux différents de raffinage.

Cotton linter	poly(DADMAC) (% massique)	Demande cationique ($\mu\text{eq/g}$ de cellulose)
Non refinery	0,02	1,3
PFI 3000	0,024	1,5
PFI 6000	0,027	1,7
PFI 10000	0,027	1,7

3.4. Potentiel Zêta des pâtes aux niveaux différents de raffinage.

La teneur des groupements anioniques augmente avec l'augmentation du nombre de rotation subi par les fibres. Les values obtenu pour les pâtes non raffinées sont en accord avec celles reportées dans la littérature pour des espèces végétales similaires [3,6,21,22].

Tableau 22 : Demande cationique des pâtes aux niveaux différentes de raffinage

Numéro de revolutions	Demande cationique ($\mu\text{eq/g}$ de cellulose)		
	Eucalyptus blanchi	Résineaux de Tarascon	Cotton linter
0	2,2	0,6	1,3
3000	7,4	3,7	1,5
6000	11,7	4,9	1,7
10000	17,0	7,4	1,7

3.5 Conclusions

L'objectif principal de notre travail a été l'étude des phénomènes d'adsorption en présence de bleu de méthylène comme colorant par spectroscopie de UV–Visible méthode et des propriétés électrocinétiques des fibres de cellulose par potentiel zêta méthode.

Pour ce faire, nous avons utilisé la méthode de spectroscopie (UV-Visible) et grâce à laquelle nous avons pu déterminer la variation des quantité de bleu de méthylène adsorbées en fonction de celles ajoutées. Aussi, nous avons utilisé la méthode de potentiel zêta de différent types de pâtes à différents degrés de raffinage. Trois pâtes sont choisi comme les pâte échantillons suivantes, eucalyptus blanchi, résineaux de Tarascon et cotton linter. Nous avons utiliser la suspension des fibres dans 0.6 mM

barbital pour contrôler le pH. La réaction est très rapide pour compléter dans 2 minutes ou 30 minutes.

Nous avons trouvé dans résultats que l'adsorption de eucalyptus blanchi, résineux de Tarascon et coton linter (non raffinage et raffinage PFI 3000, 6000 et 10000) ne peut être pas expliqué comme l'expression normal. On a pensé que l'autre model peut être montré : Langmuir. Nous avons supposé que il y un désorption sur isotherme de adsorption parce que quantité de adsorption de bleu méthylène est descendu quand le temps de réaction est plus long. En plus pour déterminer de demande cationique des pâtes par la méthode de potentiel zêta, on a trouvé que plus degré de raffinage, plus haut de cationique demande qui reflex à la quantité de groupe de anionique sauf coton linter que ce valeur est près que le même. Un raison est peut être supposé est la nature du pâte.

References :

1. Belgacem M.N. and Gandini A., 2008. , “*Monomers, polymers and composites from renewable resources*”, Elsevier, Amsterdam, The Netherland.
2. Wagberg. L and Annergren. G, Physicochemical characterization of paper making fibers , dans: *The fundamentals of papermaking material*, transaction of the 11th fundamental research symposium at Cambridge. Septembre 1997” Edit by : *Baker, C.F., Pira international, UK*, 1997.
3. Roberts.J.C., *The chemistry of paper. Departement of paper,UMIST, Manchester*,1996. .
4. Fontaille. M et Gnanou. Y, *Chimie et physicochimie des polymères*, Dunod, Paris,2002.
5. Scott. W. E, Abbott. J. C and Trosset. S, *Properties of paper: an introduction.*, TAPPI, Atlanta, Georgia, 1995.
6. Eklund. D and Lindström. T, 1991. *paper chemistry, DT Paper science publicaions, Grankulla, Finland.*
7. Lindström. T and Domsjö. M, 1992. *Nordic Pulp and Paper Research Journal* 7(4), p 181-192.
8. Onabe. F, *A systems approach to the interfacial properties in polyelectrolyte-cellulose interactions*, *thesis of University of Tokyo*,1979..
9. Schaw. D. J, *Introduction to colloid and surface chemistry*, Butterworths-Heinemann, London-UK, 1992..
10. www.metso.com
11. M. Sjöström, 1989. *Nordic Pulp and Paper Research Journal* 4(2), p 90-93.
13. Jean-Jacques Donzé, *Colorants textiles , Technique de l'ingénieur*, 1988. Ref; K-350.
14. http://en.wikipedia.org/wiki/Methylene_Blue
15. Kaewprasit,C. , Hequet, E. , Abidi N. and Gurlot J.P., *The Journal of Cotton Science* 1998, 2, p 164-173.
16. Davidson, G.F., *J. Text. Inst.*, 1948., 39, T65.
17. Fardim P. and Holmbom B. *Tappi J*, 2003, 2, 28.

18. Missaoui, PhD thesis, National Polytechnic Institute of Grenoble, France, 2005.
19. Gullichsen J. and Paulapuro H., "*Papermaking Science and Technology*", Fapet Oy, Helsinki, 1999, Vol.2 -3.
20. Kennedy J.F., Philips G.O., Williams P.A., "*The Chemistry and Processing of Wood and Plant Fibrous Materials*", Woodhead, Cambridge, UK, 1996.

CHAPTER I

STATE OF ART

Wood contains between 40 and 55% cellulose, 25 and 40% hemicellulose, 15 and 35% lignin (based on a mass dry basis) [1]. Generally, cotton is mainly composed by cellulose. Lignins are complex hydrocarbon polymer with aliphatic and aromatic moieties. Their functional groups such as conjugated carbonyl groups are responsible of the coloration of lignocellulosic-based materials. Generally, lignin macromolecules are removed during the process of chemical treatment such as cooking and bleaching.

Then the obtain products are hemicellulose, pure cellulose and oxidized cellulose which contains carboxyl group. Cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose units (for simplicity, it can be named anhydroglucose units or glucose units) which has CH_2OH and OH group and between each unit bond with ether bond where as hemicellulose composes of acid group in its structure.

In cellulosic fiber paper, carboxylic group (COOH), is the mainly group in hemicellulose, and which is more than the one in oxidized cellulose and lignin during many steps of cooking and bleaching processes. The quantity of COO^- is an important factor of the physico-chemical properties of cellulose fiber and the mechanic properties of the paper made from these materials. This parameter depends on the interactions to the cationic additives in the process of papermaking. Carboxyl group increase represent the ion-exchange capacity of pulp such as the ability of absorb metallic cations during processing. In paper pulps, COOH groups contribute to the bonding of fibers and formation of paper, and to the retention of rosin size. Contrary, the absorbed cations are largely responsible for discoloration of pulp and paper on drying. Stability and electric properties of condenser paper depend mainly on the amount of metal ions bound by the carboxyl groups. In dissolving pulps, the carboxyl groups increase viscosity and decrease pulp solubility [2]. There are several methods to determine carboxyl group which will be presented later. The methylene blue method is appropriately for low quantity of carboxyl in cellulose. The topic of thesis is adsorption of dyes to cellulose surface. The importance point of its expected reaction is on the ion exchange between methylene blue ion and carboxyl group from cellulose.

The goal of this thesis are :

1. Adsorption of methylene blue, cation dye, to the surface of cellulose in suspension of fibers of cellulose : linter cotton, bleached eucalyptus and softwood of Tarascon. Buffer, Barbitol, is applied to the system to controle the pH of suspension.
2. Determine cationic demand on cellulose fibre by zeta potential method.

Carboxyl group determination in cellulose materials

Almost methods for determining carboxyl groups in cellulose materials are based on cation exchange (1.1) where M^+ is the cation in the solution [1].



The increase of H^+ or the decrease of cation can be measured. Moreover, the estimated cation may be eluted from the neutralized cellulose acid. The corrected result should be up the right side of equilibrium. There are 3 methods are considered, alkali metric method [3], calcium exchange method [4] and methylene blue method [5]. It is necessary to convert the cellulose material into free acid form by steeping it in dilute acid and washing with deionised water before doing the ion exchange, but it is contrary to the third method.

Each method can be considered as follow:

1. Alkali method

In the theory, this method is attractive in determination of carboxyl group in cellulose without carbonyl group.

The metallic, M^+ , bound to the carboxyl groups are exchanged for hydrogen ion, H^+ , by treatment with excess acid. Then washing with water. Using alkali for neutralization of free acid form of the cellulose and the salt is performed. Some methods are based on a direct titration with alkali or addition of excess alkali and back titration with acid in the absence of the cellulose [1,3]. The difficulty of the latter case is to exclude the carbon dioxide completely of the whole experiment.

2. calcium exchange method

This method employs a dilute solution of calcium acetate buffer to achieve a final $\text{pH} \geq 6.5$. Before and after exchange by titration with ethylenediamine tetraacetic acid, EDTA, calcium can be determined [1,4]. Some part of carboxyl groups can be converted to lacton by preliminary acid washing but it does not react to $\text{Ca}(\text{OAc})_2$ and the lower result, an error, can be obtained. Lactones formation is less serious in alkali method because of its reversion under alkaline conditions [1,4].

Another method such as iodometric method can be estimated carboxyl group and the continuation of characterization of acid group can be proposed [7].

Some [8] refers to determining lactone content by iodide-iodate method after saturation of the free carboxyl with Zn^{2+} (liberation of iodine on lacton cleavage) and by coloration of the uncleaved lactone with NH_2OH and FeCl_3 . The difference between the total carboxyl group content and lactone content can be observed.

3. methylene blue method

The methylene blue, cation dye, is the chloride of the strong base (Fig. 1.1) [1]

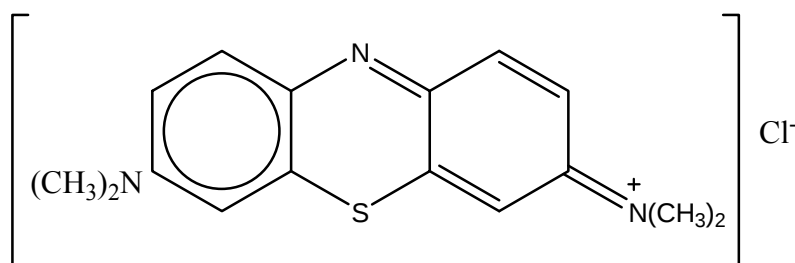


Figure 1.1 : Structure of methylene blue

As the quality of methylene blue absorption in visible range, it can be used this substance to measure its absorbance by UV-Visible spectroscopy.

The zeta potential and cationic demand can produce the parameter in the moist part of paper mill. The zeta potential may be measured to optimise the cationic filler retention and the mechanical properties of paper. The colloidal titration is based on the complexation of opposite charge of polyelectrolyte and permitted depending on the size of the titrant molecule to determine the total charge or the surface of the cellulosic materials. In the present, these techniques are some of used principle methods in paper mill for analysis of electrostatic interaction in the moist part.

The goal of our work is to study behaviour of methylene blue adsorption on to cellulose.

1.1 Pulps raw material [9,10]

- The coverslip terraced (0.5 to 2 μ m): outside of the fiber, it is composed mainly of lignin (70%) associated with various chemical elements: mainly hemicelluloses although small amounts of pectin and cellulose may be present.

- The primary wall P: it is very thin (30 to 100nm) and often confused with the adjoining strip. The filaments are few and coated in a mixture of lignin (50%), pectins and hemicelluloses.

- The secondary wall is the main part of the fiber which presents three distinct walls:

- The outer wall S1 is a thin-walled (100 to 200nm), in which the fibrils are wrapped in parallel propellers.

- The central wall S2: the wall is thicker (0.5 to 8 μ m). The fibrils are arranged in parallel propellers, whose angle in relation to the main axis of the fibre is low, the rigidity of the fiber depends on the thickness of the wall.

- The inner wall or tertiary S3 is a thin wall (70 to 100nm) and adjacent to the lumen. In this wall, the fibrils are quite heavily tilted in relation to the main axis of the fibre.

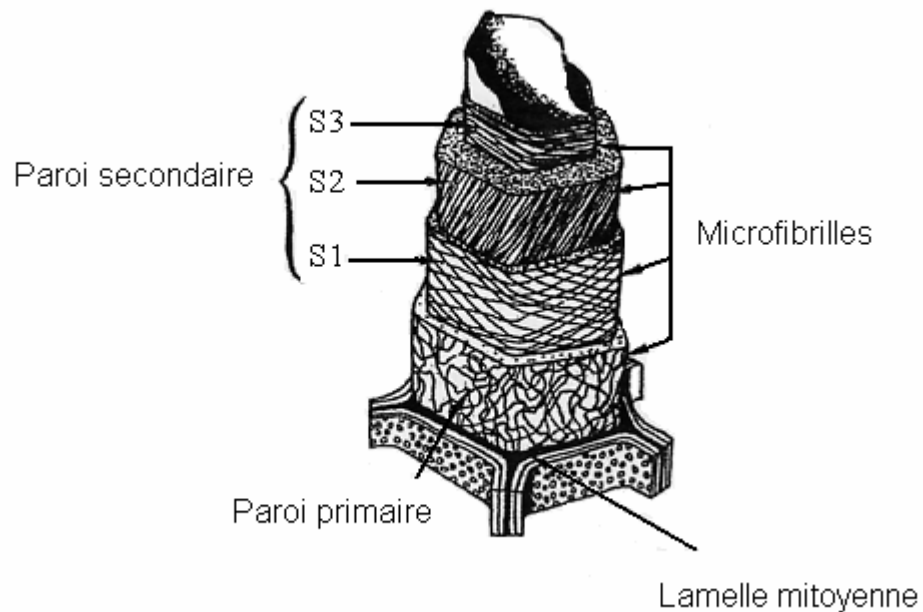


Figure 1.2 : Anatomic structure of wood [9].

Chemical composition of wood

The paper is composed mainly of vegetable fiber. Papermaking is based mainly on the filtration of a suspension of fibres diluted on a canvas, allowing for a sheet of sufficient cohesion which suffers later, for pressing and drying. Wood is the raw material most often used for the manufacture of pulp, although in some countries, annual plants may be the main source of the raw materials needed to manufacture pulp. Wood is an abundant natural materials consist of various parties (from outside to inside), including [9-11]:

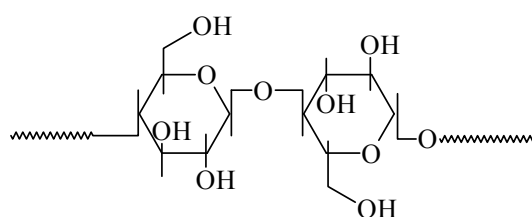
- The outer bark: (rhytidome), which plays a role in protecting wood.
- The inner bark: (vacant), which led the sap.
- The base generator: (Cambium) which produces wood cells inwards and outwards free.
- The wood itself: (xylem), which takes the form of layers corresponding to the seasonal and annual growth.

Wood is composed of different molecules and macromolecules that can be classified [12] as follows:

1. The carbohydrates which include cellulose and hemicellulose.
2. The phenolic substances which include lignins and colored substances.
3. Extracting molecules, proteins and minerals.

1.2. Cellulose

Cellulose is a natural polymer particularly important since it is the main component of plant biomass (40 to 50% of the weight of wood). Indeed, through photosynthesis, several tens of billions of tons of cellulose are produced each year. From the point of view chemical, cellulose is a polyholoside whose composition corresponds to the formula $(C_{12}H_{24}O_{10})_n$. It consists of macromolecules linear high molecular weight ($1.5 \times 10^6 - 2 \times 10^6 \text{ g.mol}^{-1}$), formed by β (1-4) bonding or more chain of glucose linked together by bonds precisely grounds cellobiose [12], as shown in (1).



(1)

The presence multiple hydroxyl group makes cellulose a molecule very hydrophilic. This property is exploited in the context paper [13-15].

The chain cellulosic may contain some grounds other than sugar glucose, mainly from xylose and arabinose. These grounds "abnormal" of the cellulose chain induce structural defects that are more easily attacked during the processing of cellulose. The

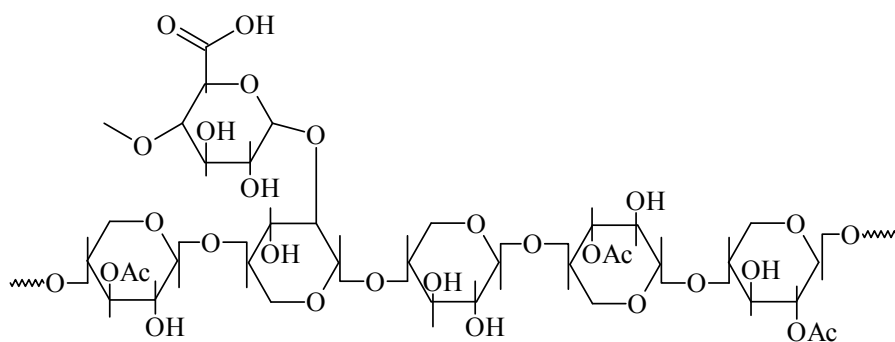
acid solutions can break the chains cellulosic providing a range of products, up glucose.

1.3. Hemicelluloses

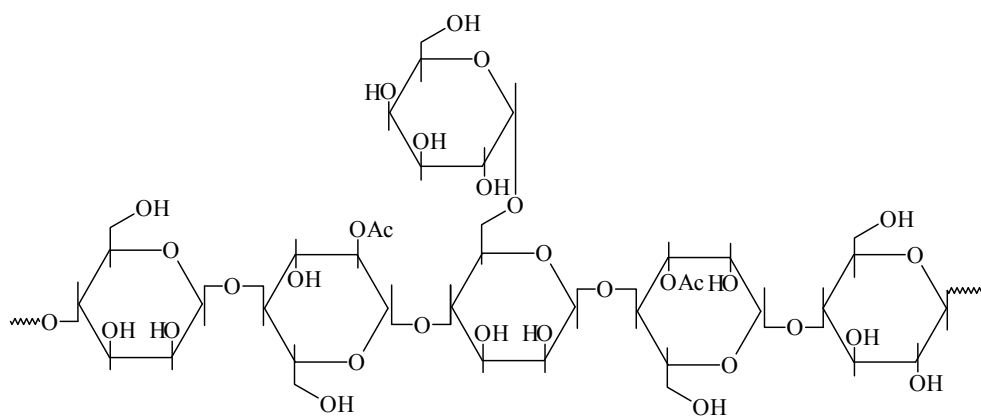
The hemicellulose are carbohydrates with a degree of polymerization average of 150, composed mainly of hexose (glucose, galactose mannose...etc) and pentoses (xylose, arabinose..... etc.). They are characterized by their structure less regular [11,12]. In nature, there are two broad categories of hemicelluloses. The first category includes hemicellulose almost linear mass molar high and with little or no carboxylic groups. The second class is characterized by branched structures whose molecular weight is lower and highest carboxyl group content [11].

The galactoglucomannane, consisting of a linear chain of glucose and α (1-6) on grounds of β (1-4) is substituted in mannose linked galactose, is the main constituent (20% of the dry mass of wood). Hemicelluloses of softwood. The arabino-(4-O-methylglucurono) xylane (5-10%), which consists of xylose units linked to β (1-4) substituted bonding by the L-arabinofuranose and acid 4-O-methylglucoronique is the second hemicellulose in the conifers.

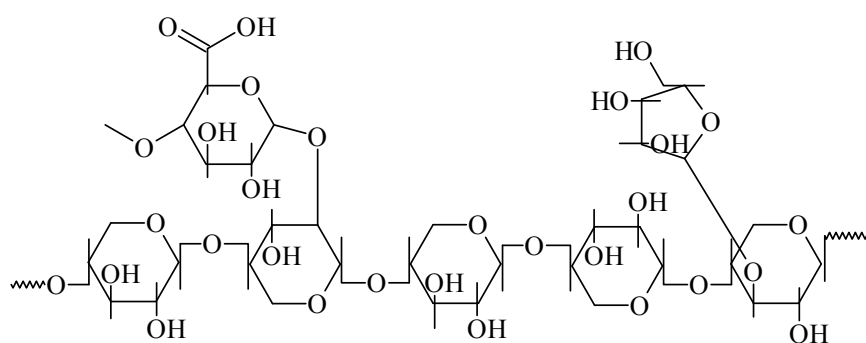
Much of hemicelluloses of hardwood is composed of glucuronoxylanes (15-30% of the dry mass of wood). These channels are composed of D-xylyose linkage in β (1-4) and substituted in α (1-2) by acid 4-O-methylglucoronique. The hardwood also contains small amounts (2 to 5%) glucomannose composed of glucose units and mannose linked by β (1-4) [12]. The formulas 2-4 show the chemical structure bonding of some hemicelluloses, taken for examples.



(2)



(3)



(4)

The hemicelluloses are very hydrophilic molecules. Their presence is essential for fiber paper because they improve significantly to the mechanical properties of paper [10] and are the main source of additives retention of the wet.

1.4. Pectic substances

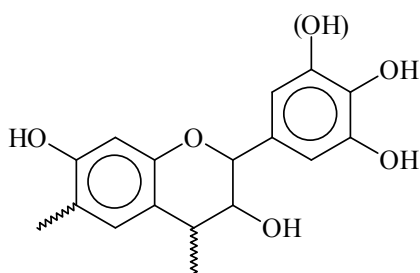
The pectin is composed mainly of polymer uronic acid. Most uroniques acid most are galacturonic acid and glucuronic acid. They are the products of oxidation of primary alcohol group of galactose and glucose.

1.5. Lignin

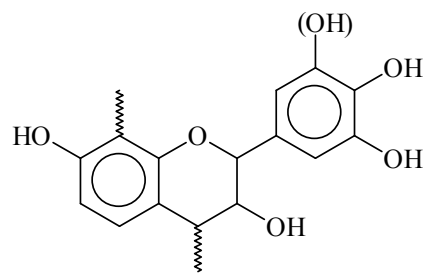
Lignin is, it is composed of 17-33% of the dry mass of wood. Lignin is a very complex aromatic polymer whose detailed chemical structure is difficult [13]. The original lignin is not a single substance, because it varies depending on the species, age and climatic and geological conditions in which the plant draws its growth [11]. Several attempts to establish the chemical structure of lignin have been postponed. The formula represents a 5 proposal fairly common and accepted by the community of chemist's wood.

1.6. The tannins and other phenolic compounds

The tannins are natural phenolic oligomers. They are present mainly in the bark of pine and mimosa. The two structures are most representative of tannins are flavonoids 4-6 and 4-8 flavonoids presented in the forms 8 and 9 [11].



(8)

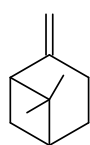


(9)

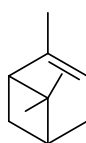
1.7. Extractable substances

They are characterized by their low molecular weight and represent a very small proportion of the total mass of wood and may contain four families:

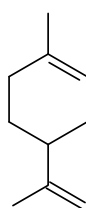
a. The terpenes, which are the most volatile. They are obtained by condensing gas cooking wood. The molecules are most representative of this family - pinene (formula 10 and 11), limonene (Form 12) and β - and α are the myrcène (Form 13).



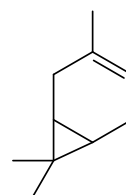
(10)



(11)

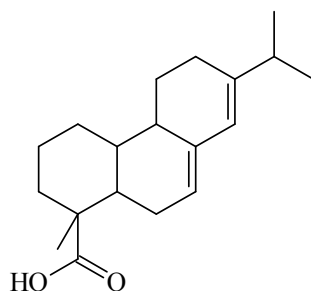


(12)



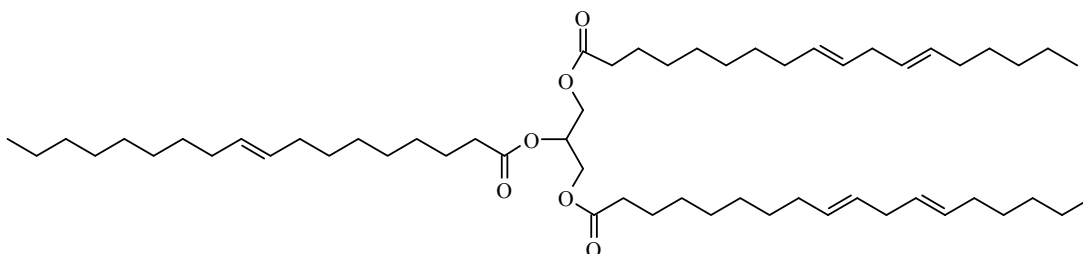
(13)

b. The resins are isomers of abietic acid (Form 14). They are isolated liqueurs cooking wood (talliques oils or "Tall oils") and may have various industrial uses (paper, stickers, etc.)..



(14)

c. The vegetable oils which are triglycerides resulting from the condensation of three fatty acid molecules with glycerol (15 formula gives an example). They can be classified into two categories: oils (fatty acids which are oil are unsaturated) non-drying (fatty acids which are oil are saturated) and drying oils. The main fatty acids that are found are palmitic acid, stearic, oleic, linoleic and linolenic éléostéarique [11].



(15)

Wood also contains a certain amount of calcium salts of magnesium and potassium [6]. Much of extractable substances and salts, is eliminated during different stages delignification and bleaching. The proportion of these remaining compounds in the pulp and paper processes depends on cooking and used laundering [12].

1.8. Dyes

1.8.1. Nomenclature and Classification

The mauvéine (used for silk and cotton) was the first synthetic dye, to be obtained by Perkin in 1856. Following this example, synthetic dyes were first baptized names of plants (amaranth, fuchsin, madder, and so on). Then the names of ore (malachite green, auramine, etc.) Dyes were then designated according to their chemical composition (methylene blue, Violet methyl naphthalene Green, etc.) [16].

1.8.2. Rankings dyes

The classification of dyes can be made according to their constitution chemical or their field of use according to the latter are the mordant dyes, acids, metal, direct, sulfur, tank and leuco-esters, reagents, intractable plastosoluble azo , pigments and cationic dyes [16].

- bite dyes: They are soluble dyes whose particularity is to be able to form complexes with metal ions, for example through two hydroxyl groups close to each other (Figure 1.3).

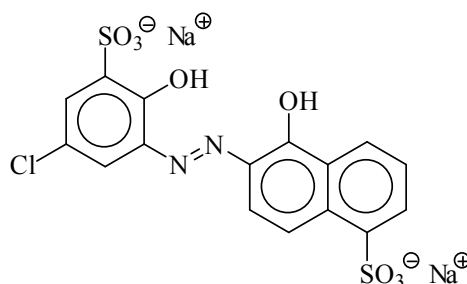


Figure 1.3: Example of a bite dye - Mordant blue 9.

- acid dyes: They are made of a chromophore group (responsible for the effect of colour) and one or more groups sulfonates allowing their solubilisation in the water. they can reach some fibre (fibre animal protein, polyamide) acid bath.

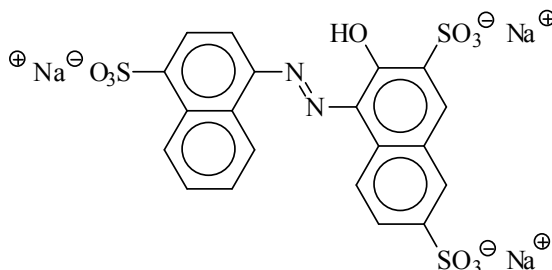


Figure 1.4: Example of a acid dye: acid red 27

- direct dyes: They differ acid dyes by their affinity for cellulosic fibers, affinity partly due to their linear form and structure of nuclei coplanar aromatic entering their constitutions.

There is also the vat dyes and their leuco-esters, reagents, intractable plastoinsoluble azo and cationic dyes.

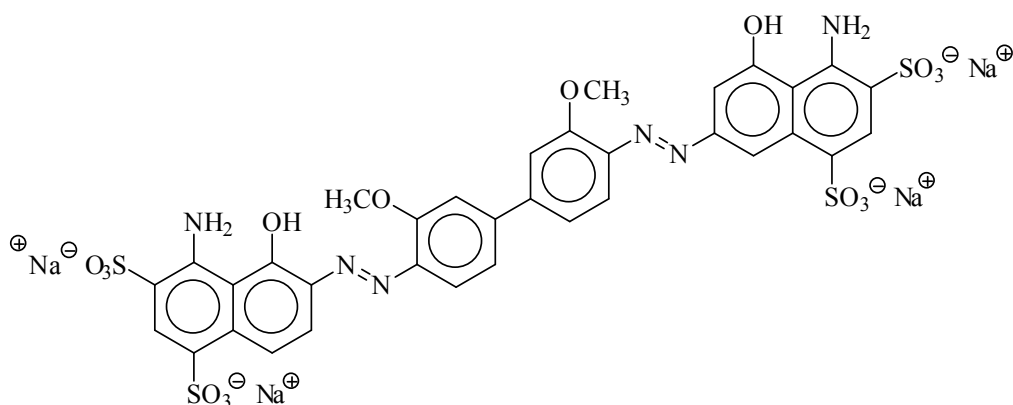


Figure 1.5: Example of a direct dye; direct Blue 1

- Cationic dyes or basic dyes: The basic dyes are cations colored dyes unlike acids, mordant and direct anions are colourful. The dye have the basic functional groups as cationic-NR₃⁺ or + = NR₂. The liveliness of colorations obtained with these dyes is remarkable; coloration intense, but in return, these products are toxic and difficult to resist the action of light, so they are no longer used for colouring natural fibres.

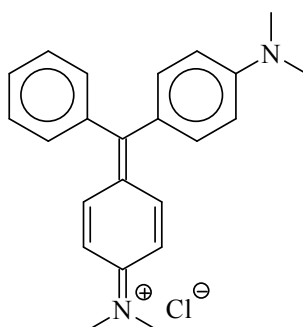


Figure 1.6: Example of a cationic dye; basic green.

1.8.3. Methylene blue

Methylene blue is a heterocyclic aromatic compound with the chemical formula bis-(dimethylamino) – 3,7 phenazathionium chloride and molecular formula: C₁₆H₁₈ClN₃S. It has many uses in a range of different fields such as biology or chemistry. At room temperature, it appears as full powder, odorless, dark-green, the structure of this dye is shown in the figure below [17].

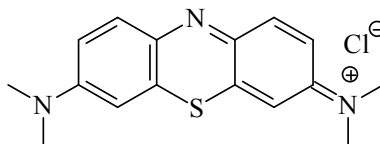


Figure 1.7: bis-(dimethylamino) – 3,7 phenazathionium chloride [17].

In addition to its various utilities in the biological and medical methylene blue is commonly used as a redox indicator in analytical chemistry, its solutions are blue in an oxidizing environment, but become colorless when they are exposed to a reducing agent.

According to experiments conducted by Froix and Nelson, 1975, the methylene blue was chosen in various studies and experiments because of its known strong adsorption on solid and its usefulness identified by characterizing the material absorptive [18]. However, the technique of methylene blue is particularly interesting because of its simplicity [3]. Many of experience using this dye for studies of the kinetics adsorption fibrous materials as sepiolite for example [19].

1.9 Electrokinetic properties of pulps

1.9.1 Charges at interface

Introduction

Generally, most substances immersed in a polar liquid acquire an electrical charge which acts on the distribution of ions in solution. Potential surface are varied to determine the energies of interaction between the particles and hence, the level of stability of the suspensions [20,21].

According to Shaw There are many mechanisms to form the electrical charge of surface, depend on the nature of substance [21] :

1. Ionization: for example, a protein is essentially acquire its charges by ionization of carboxyl and amino group to give COO^- and NH_3^+ .
2. The adsorption of ions: in the case of calcium carbonate, the charge of surface particles is due to phenomena of adsorption of ions such as Ca^{2+} , CO_3^{2-} ,.....etc. The equilibrium solubility of these particles is an importance for the amount of acquired charge.
3. Ion exchange: This is a partial substitution of certain ions by others of different valence: Si^{4+} replaced by Al^{3+} , or Al^{3+} replaced by Mg^{2+} . The deficit is made up by hydrated ions such Na^+ ou Ca^{2+} .

The theory of the electric double layer

Electric double layer constitutes the environment of is the particles in suspension. It is generally composed of two parts: the first which adjacent to the surface, containing adsorbed ions and the second in which the ions are under electrostatic interactions and thermal agitation.

In 1879, Helmholtz defines a model of interface assimilable to a capacitor plan. It assimilates the system to a layer thickness d equals to the diameter of the adsorbed ions. The density of surface charge can be written by the following equation:

$\sigma_0 = \frac{\psi_0 \varepsilon}{d}$ where $\frac{\varepsilon}{d}$, ψ and ε are the capacity of capacitor, the electric potential of surface and the permittivity, respectively.

At the beginning of the 20th century, and Chapman Gouy suggest that the thermal agitation prevents the existence of a compact electric layer by supporting the distribution of ions in the environmental medium. Thus, they postulate the existence of a diffuse ionic atmosphere. Their theory is based on the following assumption:

1. ions in solution are assimilated to concentrated charges
2. the solvent is considered as a homogeneous medium

The theory of Gouy-Chapman based on two fundamental equation, Maxwell-Boltzman equation and Poisson 's equation, which allows us to define the electric potential, ψ , according to geometrical co-ordinates and ionic concentrations.

Give ψ_0 and ψ are electric potentials on the surface of the particle and electric potentials at distance x from the surface in the electrolyte solution, respectively. If the surface is positively charged while the distribution of ions given by Maxwell's Boltzman equation:

$$n_+ = n^0 \exp \left[-\frac{ze\psi}{kT} \right] \dots\dots\dots 1$$

$$\text{and } n_- = n^0 \exp \left[+\frac{ze\psi}{kT} \right] \dots\dots\dots 2$$

where n_+ and n_- are the concentrations of positive and negative ions, respectively in a solution and the ψ is potential.

n^0 = Concentration of each species Ion infinite distance from the surface

k = Boltzmann's constant

T = temperature

e = elementary charge

z = valency counter-ion

The charge density per unit volume is defined by:

$$\rho = \sum_i z_i e n_i$$

The Poisson's equation relates to the density of volume charge, ρ , to the electric potential, ψ :

$$\nabla^2 \psi = -\frac{\rho}{\varepsilon}$$

where ε is the permittivity of medium.

2.9.2 Definitions of electrokinetic phenomenon

In the solid particle suspension, the interface (between the solid and the solution) becomes generally the place of electrostatic phenomenon due to the store of surface potential. If any parts of the electric double layer are movement in relation to each other, the electric phenomena are observed [21].

These phenomena are electrokinetics : the importance is the electrokinetic potential developed by particles carried in suspension in a liquid medium [20]. They can be distinguished according to the observed effect and the applied force :

1. Electrophoresis indicates the movement of particles compared to the liquid in a suspension in an electric field.
2. Sedimentation potential, resulting from applying an electric field in a flowing suspension (sedimentation, centrifugation).
3. Electro-osmosis, observe by a difference of electric potential, the movement of liquid compared to a solid wall (capillary tube, membrane).
4. Streaming potential which resulting from the through-flow of a fluid to a porous medium under a pressure difference.

TABLE 1.1 : Eletrokinetic phenomena

Applied force	Mobile phase	Phenomenon
electric force	particle	electrophoresis
	liquid	elecro-osmosis
	liquid	streaming potential
mechanic force	particle	sedimentation potential

Electrophoresis

Two cases are considered for spherical particles, depending on the size of them. It can be indicated by K_a , ratio of radius to thickness of double layer; If K_a is low then the particle can be assimilated to a point charge (Huckel equation), where K_a is high then the double layer is considered like plane (Smoluchowski equation).

In the case of low value of K_a , the applied Stokes law can be expressed to balance equation between the electrostatic force and the resistance to fluid applied on the particle :

$$Q_e E = 6\pi\eta v_e a \dots\dots\dots 3$$

where E , Q , v_e , a and η are the applied electric field, the quantity of charge in diffuse layer, the electrophoresis velocity, the radius of particular and the viscosity of fluid, respectively.

The electrophoretic mobility, μ_e , then, expressed in the following relation :

$$\mu_e = \frac{v_e}{E} = \frac{Q_e}{6\pi\eta a} \dots\dots\dots 4$$

The zeta potential is defined by the potential measured in terms of shear : it depends on the charge associated with the particle with the hydrodynamic direction ($+Q_e$) and that associated with the movable part of the electric double ($-Q_e$). The electric potential, ζ , is expressed then by the following relation :

$$\zeta = \frac{Q_e}{4\pi\epsilon a} - \frac{Q_e}{4\pi\epsilon\left(a + \frac{1}{K}\right)} = \frac{Q_e}{4\pi\epsilon a(1 + K_a)} \dots\dots\dots 5$$

where ϵ is the permittivity of medium.

$$\mu_e = \frac{\epsilon\zeta}{1.5\eta} \dots\dots\dots 6$$

In the case of a high value of K_a , Smoluchowski believes that the applied electric field, E , involves the movement of liquid in the diffuse part and that each elementary layer of the fluid reaches a relative velocity quickly and uniform parallel to the surface of particle. The established equilibrium between the electric force and the viscous resistance applied on the basic layer of the liquid thickness dx and a distance x of the surface of the particle becomes :

$$E\rho dx = \left(\eta \frac{dv}{dx}\right)_{x+dx} - \left(\eta \frac{dv}{dx}\right)_x = \frac{d}{dx} \left(\eta \frac{dv}{dx}\right) dx \dots\dots\dots 7$$

where ρ is the density of charge of solution.

Substituting the Poisson equation in 5, yields

$$-E \frac{d}{dx} \left(\epsilon \frac{d\psi}{dx}\right) = \frac{d}{dx} \left(\eta \frac{dv}{dx}\right) \dots\dots\dots 8$$

Set the boundary condition following :

$$\text{if } x = \infty, \text{ then } \frac{d\psi}{dx} = 0 \text{ and } \frac{dv}{dx} = 0,$$

by two integrations of equation 6 gives,

$$-E\epsilon\psi = \eta v + cste \dots\dots\dots 9$$

Finally, assume the boundary condition : $\psi = 0$, $v = 0$ if $x = \infty$ and $\psi = \zeta$, $v = -v_e$

in the terms of shear, equation 7 becomes :

$$\mu_e = \frac{v_e}{E} = \frac{\zeta\epsilon}{\eta} \dots\dots\dots 10$$

The previous expression shows that the electrophoretic mobility calculated at any point on the surface of a non-conductive particles with high K_a is independent of its size and geometric shape.

Henry proposed an equation applied to conductive and non-conductive sphere. In the terms of the limits cases envisaged by Smoluchowski and Debye-Hückel for spheres or cylinders and assuming that they are conductors, the relation can be written by :

$$\mu_e = \frac{\varepsilon\zeta}{1.5\eta} (1 + \lambda f(K_a)) \dots\dots\dots \mathbf{11}$$

where $f(K_a) = 0$ if K_a is low ,

$f(K_a) = 1$ if K_a is high.

$$\lambda = \frac{(k_0 - k_1)}{(2k_0 - k_1)} \quad \text{where } k_0 \text{ and } k_1 \text{ is the conductivity of electrolyte and the conductivity}$$

of the particle, respectively.

In the case of low values of K_a , the effect of the conductivity of the particle can be neglected. However, in the case of high value of K_a , the equation of Henry provides that the value of λ is closed to -1 and that the electrophoretic mobility is almost 0 if the conductivity of the particle is high. However, almost of cases apply an electric field to the particles possessing a character conductor results in a rapid polarization and then the particles behave as they were non-conductive.

For non-conductive spheres $\left(\lambda = \frac{1}{2} \right)$, the Henry equation becomes :

$$\mu_e = \frac{\varepsilon\zeta}{1.5\eta} f(K_a) \dots\dots\dots \mathbf{12}$$

where $f(K_a)$ varies from 1 to 1.5 corresponds to Hückel equation and Smoluchowski equation, respectively.

Streaming potential

The displacement of a liquid closed to a fixed surface and electrically charged puts moving the mobile ions of the electric double layer by giving a current or streaming flow. The equations between the current flow or the streaming potential with the zeta potential based on fluid flow in a capillary.

Give E_s , the potential difference between the two ends of an elementary capillary with radius, r and length, l under a pressure difference, Δp . In the case of laminar flow, the expression of liquid velocity, v_x with distance x from wall can be reduced to Poiseuille equation :

$$v_x = \frac{\Delta p(2rx - x^2)}{4\eta l} \dots\dots\dots 13$$

where r , l , Δp , and η are radius of capillary (m), length of capillary (m), pressure difference (Pa) and dynamic viscosity (Pa.s), respectively.

The volume of liquid velocity v_x can be regarded as hollow cylinder with radius $(r-x)$ and thickness dx . The average flow in the cylinder is given by the following expression.

$$dJ = 2\pi(r-x)v_x dx = \frac{2\pi\Delta p(2rx - x^2)(r-x)dx}{4\eta l} \dots\dots\dots 14$$

The current flow is given by the following equation :

$$I_s = \int_0^r \rho dJ \dots\dots\dots 15$$

where ρ is charge density.

The potential decreases from the surface to the electric double layer and hence where the parameter K_a is very large and if x is very small compared to the radius r , the current flow is located in an area close to the capillary wall. For a relatively large capillary, x can be neglected from $(r-x)$. By introducing the Poisson equation :

$$\frac{d^2\psi}{dx^2} = \frac{\rho}{\varepsilon} \dots\dots\dots 16$$

to equation 15, yields

$$I_s = \frac{\pi \varepsilon \Delta p r^2}{\eta l} \int_0^r x \frac{d^2 \psi}{dx^2} dx \dots\dots\dots 17$$

Given boundary condition :

$$\psi = \zeta \text{ for } x = 0$$

and

$$\psi = 0 \text{ and } \frac{d\psi}{dx} = 0 \text{ for } x = r$$

The integration of the previous equation will be written :

$$I_s = \frac{\varepsilon \Delta p A \zeta}{\eta l} \dots\dots\dots 18$$

where A is the section of the capillary.

Current flow and streaming flow are related by the following equation :

$$E_s = \frac{I_s l}{k_0 A} \dots\dots\dots 19$$

where k_0 is conductivity of suspension.

Substituting equation 18 to equation 19 gives,

$$E_s = \frac{\varepsilon \Delta p \zeta}{\eta k_0} \dots\dots\dots 20$$

k_0 can be corrected by k_s , conductivity to the surface :

$$E_s = \frac{\varepsilon \Delta p \zeta}{\eta \left(k_0 + \frac{2k_s}{r} \right)} \dots\dots\dots 21$$

In the case of porous material, it is very difficult to find a satisfied method to correct the value of streaming potential by supposing value of conductivity of material surface. By solving equation 21 where r is the average radius of pores, gave very low value of zeta potential. The effect of the conductivity of surface can be studied qualitatively by comparing the ratio of the conductivity of solution with that of the material for two different concentrations in electrolyte. Thus, the known conductivity of surface is not required to express current flow based on zeta potential. For the porous material case can be more complicated if :

1. the effective surface of mattress for current flow is different from the one exposed to fluid flow.
2. the mattress is compressible due to a variation of pore size by applying a different pressure.

This may be the cause of the valid values of zeta potential calculated from porous mattresses using this method.

CHAPTER II

EXPERIMENT

2.1 Pulps suspensions

2.1.1 Chemicals

1. Bleached eucalyptus
2. Softwood of Tarascon
3. Bleached linter cotton
4. Distilled water
5. Deionized water (DI water)
6. Anhydrous pellets NaOH
(ACS-ISO-For analysis) Carlo Erba, Italy
7. 5,5-Diethyl barbituric acid
(barbital) Fluka, Germany
(puriss grade)

2.1.2 Instruments

1. Disintegration machine, Lhomergy
2. Beating PFI mill machine
3. Magnetic stirrer
4. pH meter

2.1.3 Preparation of pulps suspensions

Three different fibrous materials were used as the raw materials investigated,

1. Hardwood bleached kraft pulps (Eucalyptus)
2. Softwood bleached kraft pulps (supplied by Tarascon mill)
3. Linter cotton

30 g of oven dried pulps were soaked in deionized water for 16 hours. The soaked pulp suspension was disintegrated using a commonly used laboratory mixing device (Lhomergy). This operation was carried out for 500 rounds and aimed at the individualization of the fibres. These pulps will be designed as non-refined pulps

throughout the present manuscript. Then, pulps with three refining levels were prepared using a laboratory PFI. Thus, the following pulps will be tested:

1. Non-refined pulps: those submitted to disintegration using Lhomergy.
2. Refined pulps: those which were submitted to PFI treatments, using 3000, 6000 and 10000 revolutions, respectively.

The consistency of the all pulps suspensions investigated was 1 g/L in 0.6 mM barbital (respect to O.D. pulps). Thus, the pulps fibres recovered from the PFI refiner and non refiner were diluted up to 3 litres using the buffer solution, 0.6 mM barbital, described below. The use of the buffer solution (see Section 2.2) aimed at maintaining a constant pH during the sorption measurements. In fact, adsorption and electrokinetic phenomena depend strongly on the pH of the reaction media.

2.2 Preparation of solutions

1. NaOH 2M was prepared by dissolving a weighted quantity of NaOH in DI water.
2. Buffer 0.6 mM in 0.4 mM NaOH barbital was prepared by dilution of the solution of 0.06 M barbital in 0.04 M NaOH.
3. 3.82×10^{-4} M methylene blue in 0.6 mM barbital was prepared by dissolving an exactly quantity of dried methylene blue with 0.6 mM barbital.
4. Stock 7.63×10^{-3} M methylene blue in 0.6 mM barbital, 20C, was obtained by dissolving an exactly quantity of dried methylene blue with 0.6 mM barbital.
5. Diluted methylene blue solutions 2C, 5C, 7C, 10C and 15C were obtained by dilution of stock solution of 7.63×10^{-3} M methylene blue in 0.6 mM barbital.
6. Solution of 0.1% (w/w) poly(DADMAC) was prepared by dissolving a quantity of poly(DADMAC) in DI water.
7. Solution NaCl 0.1 M was prepared by weighted quantity of NaCl in DI water.

2.3 Methylene blue adsorption by UV-Visible measurements

2.3.1 Chemicals

1. Methylene blue (puriss grade) Fluka, Switzerland
2. Anhydrous pellets NaOH Carlo Erba, Italy
(ACS-ISO-For analysis)
3. 5,5-Diethyl barbuturic acid Fluka, Germany
(puriss grade)
4. DI water
5. Distilled water
6. Bleached eucalyptus (non refinery)
7. Bleached eucalyptus (refinery PFI 3000)
8. Bleached eucalyptus (refinery PFI 6000)
9. Bleached eucalyptus (refinery PFI 10000)
10. Softwood of Tarascon (non refinery)
11. Softwood of Tarascon (refinery PFI 3000)
12. Softwood of Tarascon (refinery PFI 6000)
13. Softwood of Tarascon (refinery PFI 10000)
14. Bleached linter cotton (non refinery)
15. Bleached linter cotton (refinery PFI 3000)
16. Bleached linter cotton (refinery PFI 6000)
17. Bleached linter cotton (refinery PFI 10000)

2.3.2 Instruments

1. UV-VIS spectrophotometer, UNICAM UV 50
2. Beating PFI mill machine

2.4 Calibration curve for methylene blue adsorption by UV-Visible spectroscopy

A calibration curve was built by diluting of 3.82×10^{-4} M methylene blue (see section 2.2) to different concentrations in 0.6 mM barbital. The experiments were carried out immediately at λ_{max} of 664 nm by W lamp. Aluminium foil sheets were used to prevent the error absorbance from sunlight.

2.5 Adsorption Isotherms by UV-Visible spectroscopy

Take 500 ml of pulp suspension (see section 2.2) to a metallic vessels, then add 0.6 mM barbital 100 ml and stir to homogenize. The suspension was filtered twice through a sinter glass number 2. Then a double filtrate of fibrous suspension was used as reference for measurement by UV-Visible spectroscopy at 664 nm. The reactions were performed by adding 50 ml of various methylene blue concentrations, 2C, 5C, 7C, 10C, 15C, and 20C, respectively. The reaction time at 5 minutes and 30 minutes were chosen for all experiments and carried out by measurement of a double filtrate.

2.6 Zeta potential measurement

The apparatus used to measure the zeta potential of the fibrous suspensions under investigation is a SZP-04 equipment based on measuring the streaming potential. A sample of fibrous suspension (1% w/w with respect to o.d. pulps) was filtered to form a wet fibre mat at the surface of the electrode gird. When the fibre mat is formed, the vacuum is switched on to impose a drop of pressure in the range between -0.2 and -0.4 bars. The application of the vacuum induces a water circulation which displace the counter-ions within the fibre mat, thus allowing the creation of a streaming potential between the two electrodes (electrode gird and electrode ring (see Figure 2.1).

The zeta potential value is deduced measuring the following parameters:

- Streaming Potential.
- Conductivity.
- Pressure difference.

The zeta potential is calculated using Helmholtz-Smoluchowski formula:

$$\zeta = \frac{4\pi\eta U \chi G}{\varepsilon \Delta P} \dots\dots\dots 1$$

where:

- η = viscosity of water (1mPa.s at 20°C).
- ε = dielectric constant (F/m) (80.20 at 20°C, [22]).
- χ = electrical conductivity of the fibres' suspension (S/m).
- U = streaming potential (mV).
- Δp = pressure difference (Pa).
- ζ = zeta potential of the fibres in the suspension (mV).
- G = constant related to the used apparatus.

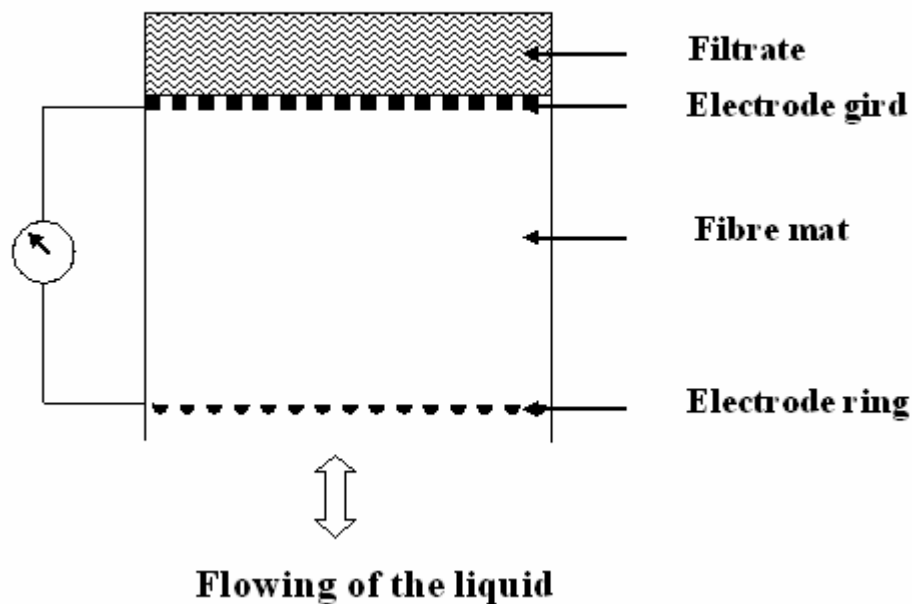


Figure 2.1 : Principle of measurements of the zeta potential apparatus (SZP04).

A previous study in our laboratory [9] has revealed that this apparatus is equipped neither with a thermocouple nor with a viscosity measurement device. It assumed that the temperature at which the experiments is carried out is 20°C and that the viscosity of water is 1 mPa.s. That is why the measured value of zeta potential were corrected [9] both in terms of viscosity and electrical conductivity. Thus the real values of these two parameters were introduced into the following Equation, which gives the corrected values of zeta potential:

$$\zeta_{real} = \frac{\eta_{real} \chi_{real}}{0,001 \chi_{ap}} \zeta_{ap} \dots\dots\dots 2$$

where :

- ζ_{real} : real zeta potential.
- ζ_{ap} : measured zeta potential by the SZP-04 apparatus.
- η_{real} : viscosity of water at experimental temperature
- χ_{ap} : conductivity (measured by the SZP-04 apparatus)
- χ_{real} : conductivity (measured by a conductimetric device *JENWAY 4330*)

The experimental conditions to measure the zeta potential were optimised by Missaoui [9]. Particularly, the electrical conductivity of the suspensions, which plays an important role since screening phenomena could take place and affect significantly the zeta potential values. In our work, a 0.1M NaCl solution was added in order to maintain the electrical conductivity of the suspensions at the values recommended by Missaoui [9], i.e., range values between 450 and 660 $\mu\text{S/cm}$.

Concretely, 30 ml of 0.1 M NaCl solution were added to the fibrous suspensions having 1% of consistency (5g of o.d. of the chosen pulps in 500 ml buffer solution). Then, increasing amounts of poly(DADMAC) were added . The ensuing suspensions were maintained under gentle stirring for 15 minutes, before measuring the zeta potential. The zeta potential of the three pulps refined at different refining levels was tested.

CHAPTER III

Results and Discussions

3.1 Methylene blue sorption on cellulose with non refinery pulps and refinery pulps with different beatings at room temperature

This experimental section related to study the effect of degree of beating of pulps to sorption of methylene blue. Unbeaten and three different levels of beaten pulps of bleached eucalyptus, linter cotton and softwood of Tarascon were studied. All experiment was performed during 5 and 30 minutes and used the same calibration curve to evaluate the sorption of methylene blue for all this manuscript.

Primary experiment, we try to find $\lambda_{\max}$ of absorbance which are shown in Figure 3.1 which presented at 664 nm.

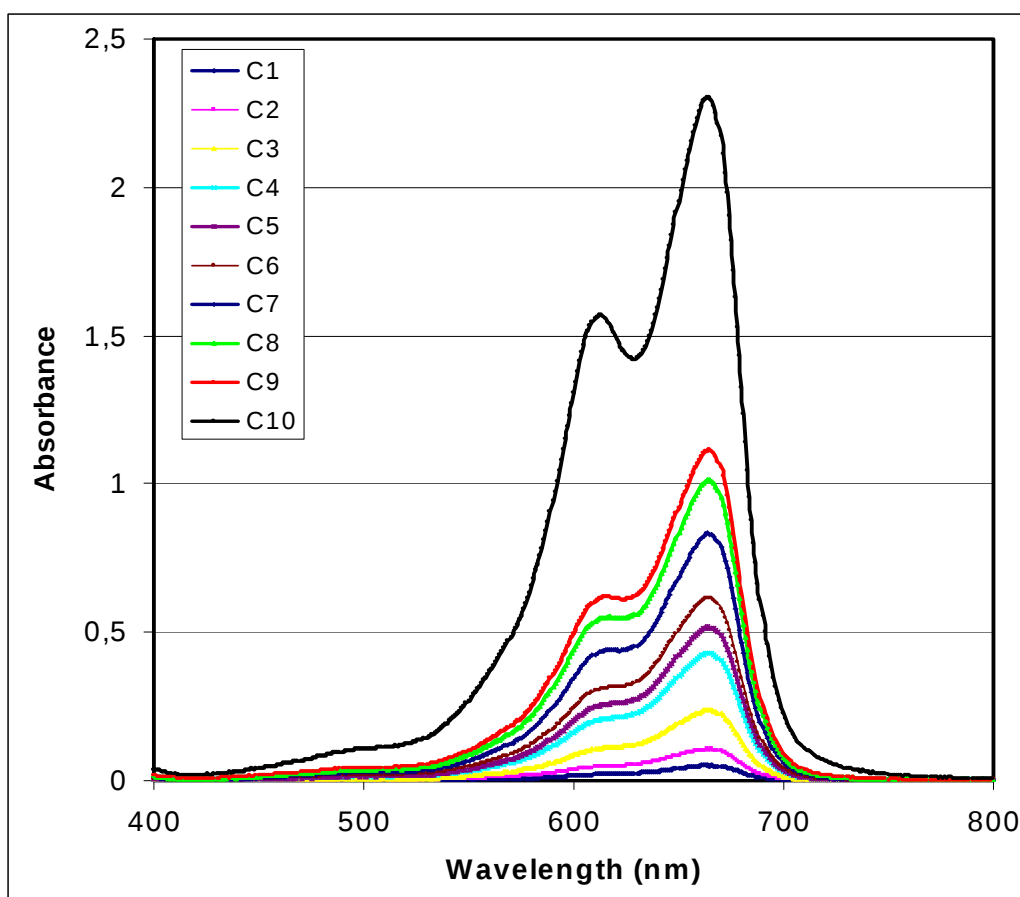


Figure 3.1 : Visible spectra of methylene blue

3.2 calibration curve of methylene blue

The calibration curve between absorbance and concentration of methylene blue, Figure 3.2 and the corresponded data are shown in Table 3.1. This curve was used all experiment of thesis for methylene blue adsorption by UV-Visibile spectroscopy. Note that the weight of dried methylene blue can be calculated after lyophilization.

Table 3.1 : Absorbance of methylene blue for calibration curve

Methylene blue concentration ($\mu\text{mol/L}$)	Absorbance
0.00	0.00
1.53	0.11
3.05	0.24
7.63	0.58
15.26	1.13

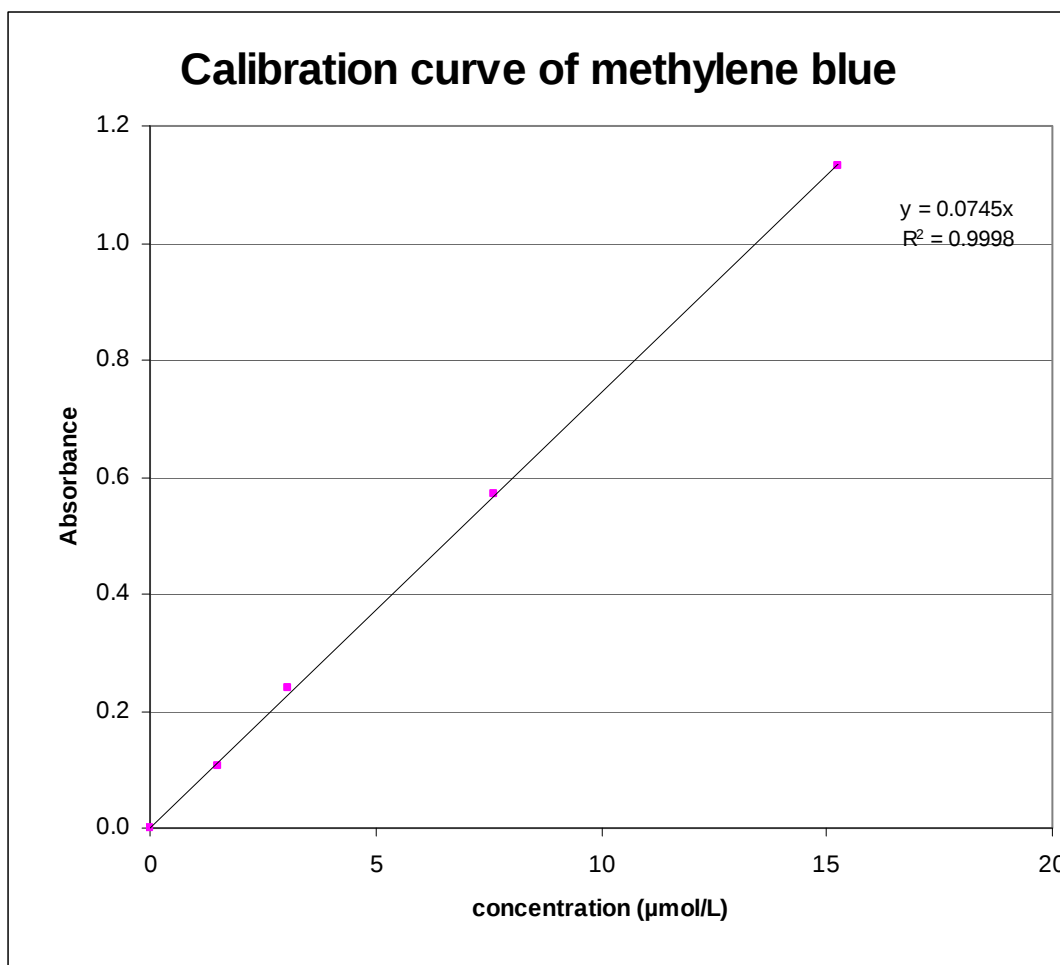


Figure 3.2 : Methylene blue absorption curve

The calibration curve of absorbance vs. concentration of methylene blue related to the equation $y = 0.0745x$, where x and y are concentration and absorbance of methylene blue, respectively. The correlation coefficient is close to the unity, $R^2 = 0.9998$. Moreover, the straight line correlating concentration and the absorbance pass through the origin (0,0), predicting that for all small concentration solutions, the absorbance measurements accuracy is quite good. This is an important issue in our study, since the dosage of methylene blue is based on its quantification in the filtrate which has no adsorbed methylene blue. Thus, the first point related to adsorption isotherm involves practically full adsorption methylene blue and remaining quantities are too small and requires good accuracy for the low concentration of methylene blue from the curves.

By our primarily experiments, the methylene blue adsorption on to unbeaten bleached eucalyptus in the suspension of fibrous by using DI water as the medium. The double filtrates of suspension were carried out during 2, 5, 15, 30 minutes and more than 16 hours for the methylene concentration of C, 2C, 5C, 7C and 10C, respectively. The adsorption isotherm is shown in Figure 3.3.

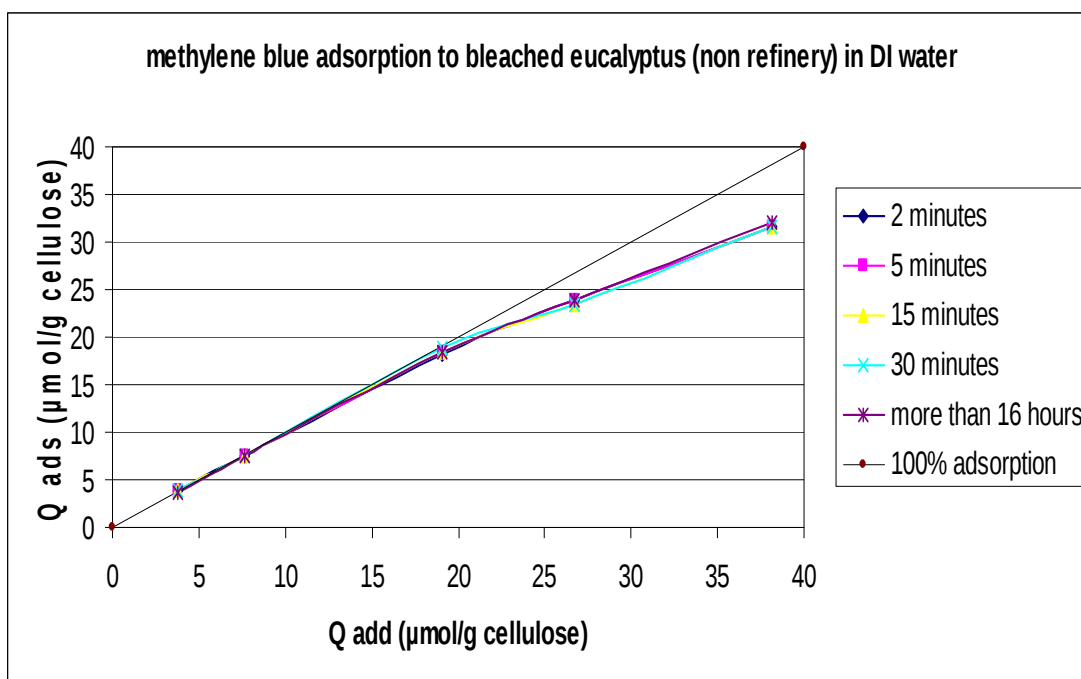


Figure 3.3 : methylene blue adsorption to bleached eucalyptus (none refinery) in DI water.

From this figure shows that the absorbance of methylene blue was stable for very low concentration of methylene blue such C and 2C which present 100% adsorption of dye. It is obviously that the higher concentrations such 5C, 7C and 10C, the adsorption are deviated from the straight line. To find the reason of this question, we found that the absorbance for very high methylene blue concentration (Absorbance > 1). Moreover, this figure shows clearly that the adsorption of methylene blue was stable during the reaction time, even though after 16 hours which is close to the beginning of reaction time. This is why we carry out the absorbance of

methylene blue for other experiments during 2 minutes and 30 minutes to confirm for refinery bleached eucalyptus PFI 3000, 6000 and 10000. Their adsorption isotherms are presented in Figure 3.4- 3.7.

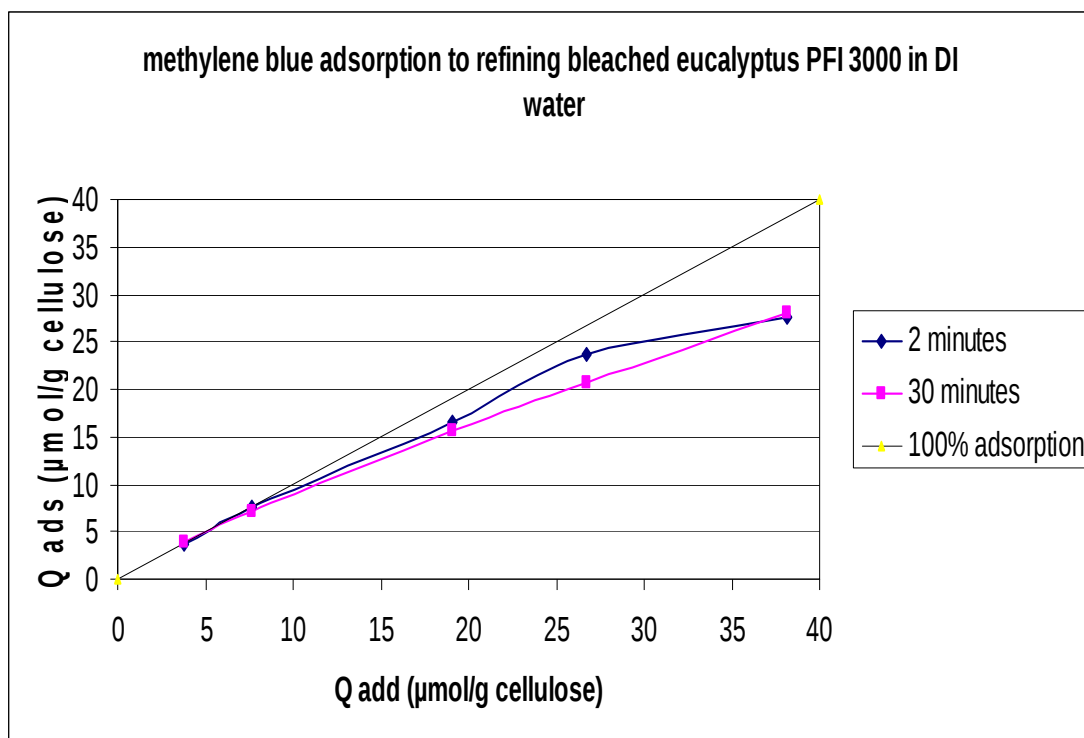


Figure 3.4 : methylene blue adsorption to refining bleached eucalyptus PFI 3000 in DI water.

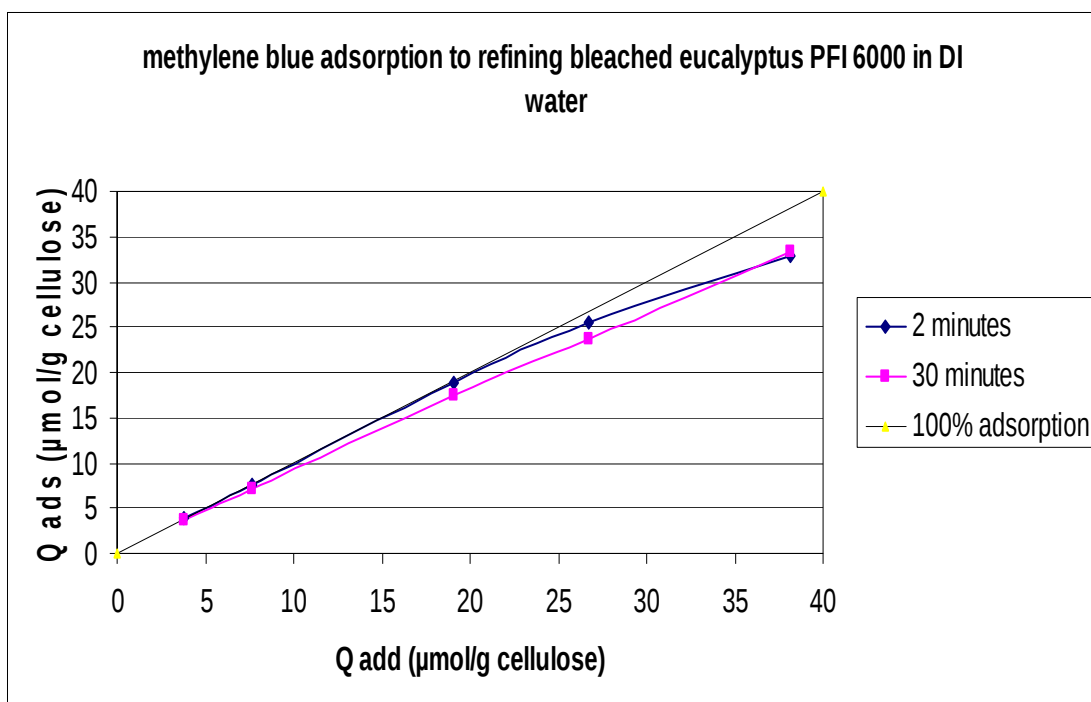


Figure 3.5 : methylene blue adsorption to refining bleached eucalyptus PFI 6000 in DI water.

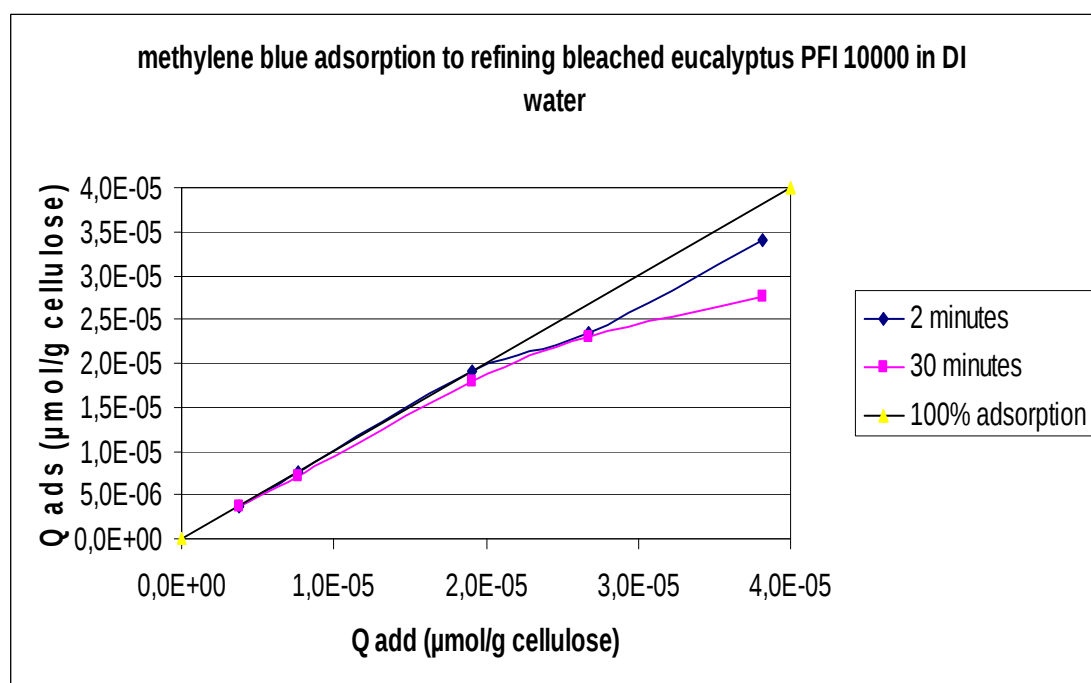


Figure 3.6 : methylene blue adsorption to refinery bleached eucalyptus PFI 10000 in DI water.

The methylene blue adsorption curve of refinery bleached eucalyptus PFI 3000, 6000 and 10000 as presented above implied that the sorption is completed within 2 minutes. The adsorption during 30 minutes of unbeaten and beaten bleached eucalyptus was chosen to build the curve as Figure 3.7 and the corresponding data are presented in Table 3.2. This implies that the completed reaction can be occurred to very low concentration of methylene blue such C and 2C. For very high concentration, increasing the concentration, the sorption is reduced. We cannot describe this result many much. One can observed from the raw data of absorbance > 1 , then why we decided to dilute the filtrate for the case of higher concentration of methylene blue such 7C, 10C, 15C and 20C. It depends on the experimental absorbance to each pulp or each level of beating pulps. Moreover, we applied the solution of 0.6 mM barbital in to the suspension of fibrous pulps to control pH. As the previous workers [23], the buffer was used as a medium of heterogeneous system of pulps while our work has been done in homogeneous system (suspension of fiber), applied from the thesis work of Missaoui [9]. The degree of beaten pulps will be compared and discussed in the next section.

The comparative medium maybe discussed in the term of ionization of media solution later.

Table 3.2 : Methylene blue adsorption on to bleached eucalyptus in DI water during 30 minutes

Type of pulp	Concentration of methylene blue (M)	Q add ($\mu\text{mol/g}$ cellulose)	Q ads ($\mu\text{mol/g}$ cellulose)	% adsorption
Bleached eucalyptus (non refinery)	C	3.82	3.78	99.18
	2C	7.63	7.20	94.35
	5C	19.08	17.47	91.58
	7C	26.71	23.76	88.95
	10C	38.16	33.31	87.30
Bleached eucalyptus PFI 3000	C	3.82	3.89	101.84
	2C	7.63	7.21	94.42
	5C	19.08	15.72	82.39
	7C	26.71	20.72	77.57
	10C	38.16	27.98	73.31
Bleached eucalyptus PFI 6000	C	3.82	3.78	99.18
	2C	7.63	7.20	94.35
	5C	19.08	17.47	91.58
	7C	26.71	23.76	88.95
	10C	38.16	33.31	87.30
Bleached eucalyptus PFI 10000	C	3.82	3.73	97.85
	2C	7.63	7.11	93.11
	5C	19.08	17.96	94.15
	7C	26.71	23.00	86.09
	10C	38.16	27.68	72.54

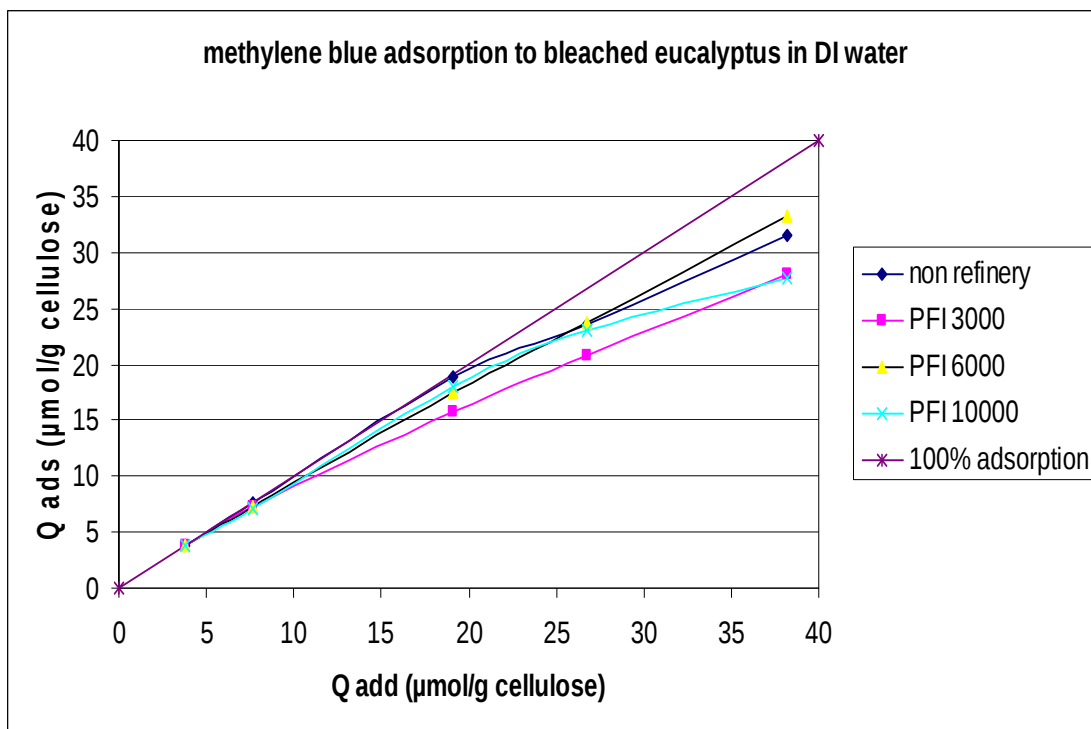


Figure 3.7 : Comparison of methylene blue adsorption on to bleached eucalyptus at different degrees of beating : 30 minutes

Three pulps, bleached eucalyptus, linter cotton and softwood of Tarascon of beating by PFI mill, 30000, 6000, and 10000 are studied in suspension of fiber when 0.6 mM was used as a buffer. The corresponded data are concluded in Table 3.3-3.5.

Table 3.3 : Methylene blue adsorption on to bleached eucalyptus in buffer system

Type of pulp	Concentration of methylene blue (M)	Time (minutes)	Q add ($\mu\text{g/mol}$ cellulose)	Q ads ($\mu\text{g/mol}$ cellulose)	% adsorption
Bleached Eucalyptus (non refinery)	2C	5	7.64	7.29	95.52
		30	7.64	7.45	97.53
	5C	5	19.09	18.42	96.52
		30	19.09	18.90	98.98
	7C	5	26.71	20.40	76.40
		30	26.71	26.32	98.54
	10C	5	38.15	29.07	76.20
		30	38.15	34.79	91.19
	15C	5	57.23	37.37	65.30
		30	57.23	41.74	72.92
	20C	5	76.31	44.27	58.01
		30	76.31	45.84	60.07
Bleached eucalyptus (PFI 3000)	2C	5	7.38	7.44	96.64
		30	7.63	7.44	97.42
	5C	5	19.08	15.19	79.59
		30	19.08	15.62	81.88
	7C	5	26.71	18.10	67.77
		30	26.71	19.94	74.64
	10C	5	38.16	25.59	67.05
		30	38.16	27.11	71.06
	15C	5	57.23	27.55	48.13
		30	57.23	27.72	48.44
	20C	5	76.31	21.57	28.26
		30	76.31	23.40	30.67
Bleached eucalyptus (PFI 6000) eucalyptus	2C	5	7.64	7.37	96.43
		30	7.64	6.81	89.11
	5C	5	7.64	6.81	85.62
		30	19.10	15.68	82.09
	7C	5	26.74	22.16	82.88
		30	26.74	22.31	83.42
	10C	5	38.20	31.84	83.34
		30	38.20	31.85	83.38
	15C	5	57.23	4.50	7.86
		30	57.23	1.62	2.83
	20C	5	76.31	2.27	2.98
		30	76.31	-2.53	-3.31

Type of pulp	Concentration of methylene blue (M)	Time (minutes)	Q add ($\mu\text{mol/g}$ cellulose)	Q ads ($\mu\text{mol/g}$ cellulose)	% adsorption
Bleached eucalyptus (PFI 10000)	2C	5	7.64	7.54	98.72
		30	7.64	7.46	97.69
	5C	5	19.10	16.76	87.73
		30	19.10	17.31	90.65
	7C	5	26.71	25.00	93.59
		30	26.71	26.39	98.82
	10C	5	38.15	34.05	89.25
		30	38.15	35.97	94.28
	15C	5	57.23	43.87	76.66
		30	57.23	40.99	71.63
	20C	5	76.31	45.67	59.84
		30	76.31	47.94	62.82

Table 3.4 : Methylene blue adsorption on to softwood of Tarascon in buffer system

Type of pulp	Concentration of methylene blue (M)	Time (minutes)	Q add ($\mu\text{mol/g}$ cellulose)	Q ads ($\mu\text{mol/g}$ cellulose)	% adsorption
softwood of Tarascon (PFI 3000)	2C	5	7.63	7.19	94.19
		30	7.63	7.45	97.62
	5C	5	19.08	16.23	85.08
		30	19.08	16.48	86.36
	7C	5	26.71	20.91	78.30
		30	26.71	22.36	83.72
	10C	5	38.16	23.49	61.56
		30	38.16	24.02	62.94
	15C	5	57.24	13.06	22.82
		30	57.24	26.42	46.16
	20C	5	76.32	9.01	11.80
		30	76.32	21.05	27.59
softwood of Tarascon (PFI 6000)	2C	5	7.63	7.47	97.90
		30	7.63	7.65	100.21
	5C	5	19.08	14.99	78.59
		30	19.08	15.13	79.32
	7C	5	26.71	21.26	79.57
		30	26.71	25.32	94.77
	10C	5	38.16	20.92	54.81
		30	38.16	20.22	52.98
	15C	5	57.24	29.30	51.19
		30	57.24	27.29	47.68
	20C	5	76.32	19.31	25.30
		30	76.32	22.36	29.30

Type of pulp	Concentration of methylene blue (M)	Time (minutes)	Q add ($\mu\text{mol/g}$ cellulose)	Q ads ($\mu\text{mol/g}$ cellulose)	% adsorption
softwood of Tarascon (PFI 10000)	2C	5	7.63	6.49	85.06
		30	7.63	5.82	76.23
	5C	5	19.08	14.28	74.83
		30	19.08	13.89	72.82
	7C	5	26.71	18.24	68.30
		30	26.71	17.54	65.68
	10C	5	38.16	14.89	39.03
		30	38.16	21.70	56.87
	15C	5	57.24	25.20	44.02
		30	57.24	27.12	47.38
	20C	5	76.32	15.64	20.49
		30	76.32	25.86	33.88

Table 3.5 : Methylene blue adsorption on to linter cotton in buffer system

Type of pulp	Concentration of methylene blue (M)	Time (minutes)	Q add ($\mu\text{mol/g}$ cellulose)	Q ads ($\mu\text{mol/g}$ cellulose)	% adsorption
Linter cotton (none refinery)	2C	5	7.63	4.78	62.70
		30	7.63	4.14	54.24
	5C	5	19.08	2.70	14.15
		30	19.08	3.55	18.63
	7C	5	26.71	2.13	7.98
		30	26.71	4.75	17.79
	10C	5	38.15	4.80	12.59
		30	38.15	5.85	15.34
	15C	5	57.23	-47.54	-83.06
		30	57.23	7.73	13.50
	20C	5	76.31	0.18	0.23
		30	76.31	3.76	4.92
Linter cotton (PFI 3000)	2C	5	7.63	4.07	53.33
		30	7.63	3.93	51.50
	5C	5	19.08	4.15	21.76
		30	19.08	4.94	25.88
	7C	5	26.72	4.36	16.34
		30	26.72	4.23	15.85
	10C	5	38.16	4.25	11.13
		30	38.16	6.17	16.16
	15C	5	57.25	-0.11	7.27
		30	57.25	0.06	7.27
	20C	5	76.36	5.99	7.85
		30	76.36	5.82	7.62

Type of pulp	Concentration of methylene blue (M)	Time (minutes)	Q add ($\mu\text{mol/g}$ cellulose)	Q ads ($\mu\text{mol/g}$ cellulose)	% adsorption
Linter cotton (PFI 6000)	2C	5	7.63	3.5	46.02
		30	7.63	4.2	55.63
	5C	5	19.08	7.7	40.44
		30	19.08	6.3	33.21
	7C	5	26.72	7.9	29.75
		30	26.72	4.9	18.31
	10C	5	38.18	3.5	9.22
		30	38.18	7.5	19.62
	15C	5	57.25	4.3	7.59
		30	57.25	5.4	9.42
	20C	5	76.36	5.5	7.16
		30	76.36	11.8	15.39
Linter cotton (PFI 10000)	2C	5	7.63	2.64	34.58
		30	7.63	4.26	55.85
	5C	5	19.08	0.71	3.72
		30	19.08	3.66	19.19
	7C	5	26.72	4.94	18.47
		30	26.72	4.24	15.86
	10C	5	38.16	1.45	3.79
		30	38.16	2.93	7.68
	15C	5	57.26	-2.03	-3.54
		30	57.26	2.25	3.93
	20C	5	76.32	2.63	3.45
		30	76.32	16.60	21.75

The methylene blue adsorption to non refining and refining of bleached eucalyptus softwood of Tarascon and linter cotton at 3 degrees of beating : 3000, 6000, 10000 in buffer system are shown in Figure 3.8-3.21.

Bleached eucalyptus

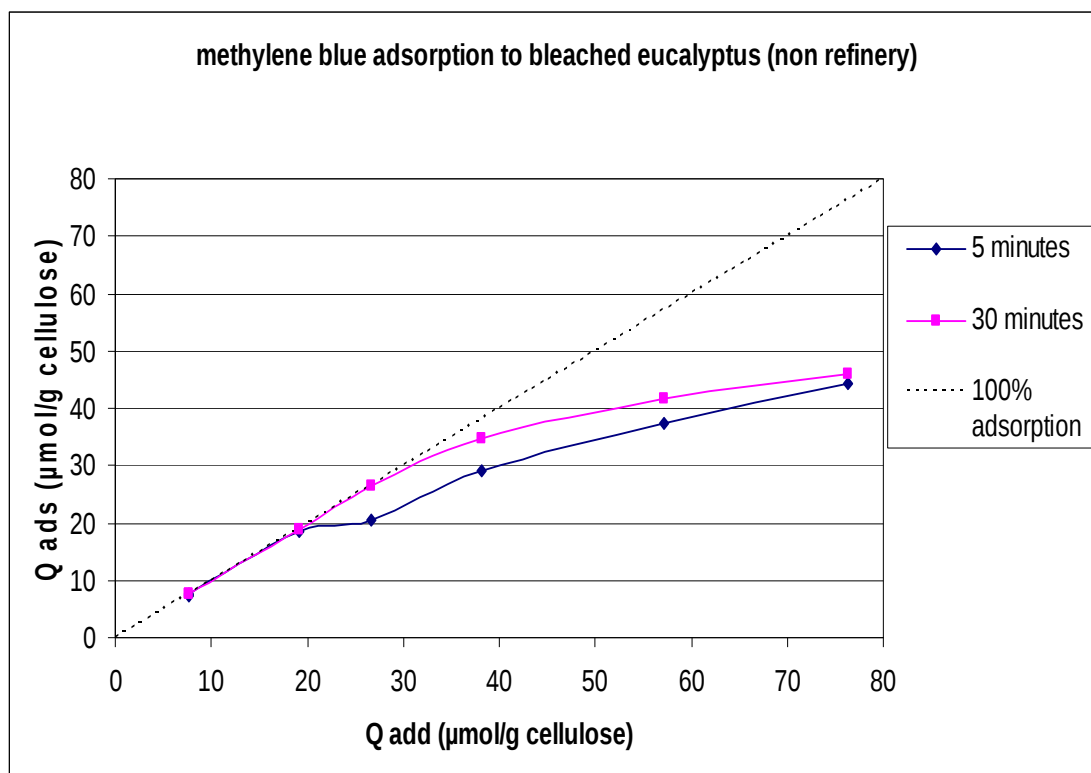


Figure 3.8 : metylene blue adsorption on to bleached eucalyptus (non refinery)

From the results in Figure 3.8, it is shown that the sorption is stable and completed during the reaction time for very low concentration of methylene blue at beginning of reaction such 2C and 5C. In the case of higher concentration, the methylene blue adsorption was reduced, there is not clearly reason to describe this appearance. Possibly reasons, desorption of methylene blue which is occurred rapidly and we did not study in kinetic field. This can be observed from the adsorption isotherms for 5C, 7C and 10C, we have not a clearly explanation. Desorption may be the one reason of this occurrence.

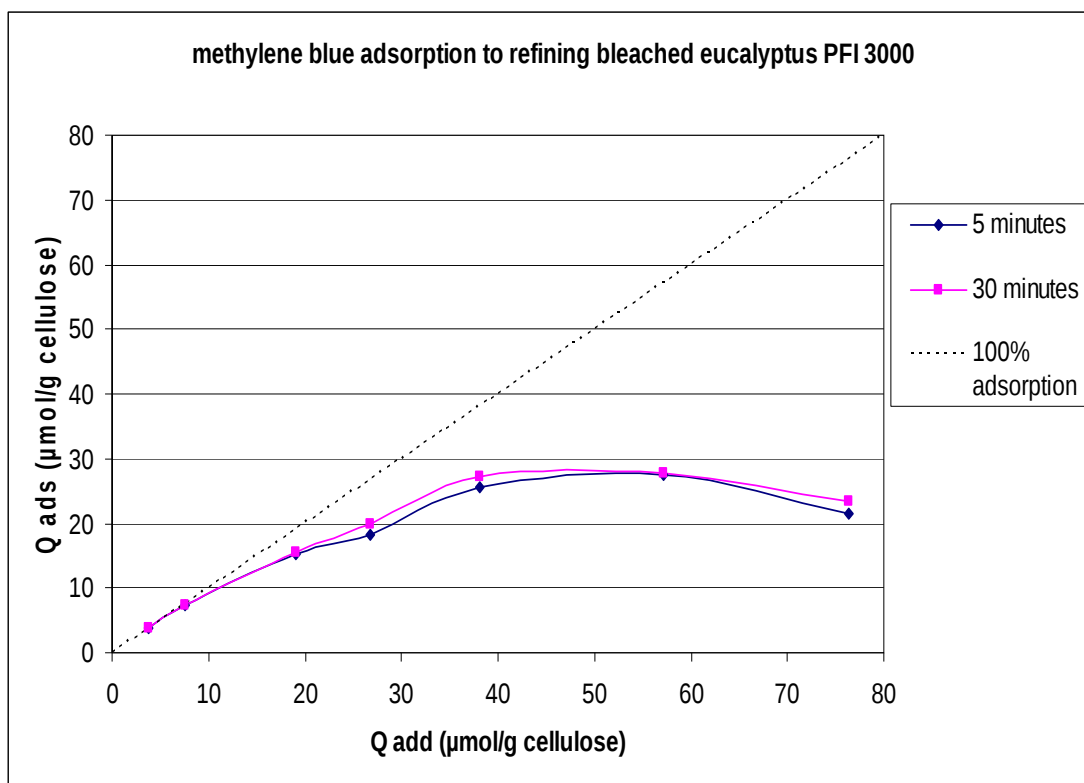


Figure 3.9 : methylene blue adsorption on to refinery bleached eucalyptus PFI 3000

From the result as shown in Figure 3.9, it is shown that the sorption on to refinery bleached eucalyptus PFI 3000 for any concentration during 5 minutes is very close to that of 30 minutes, we cannot describe these results in the term of desorption because of insufficient kinetic experiment to distribute at this point.

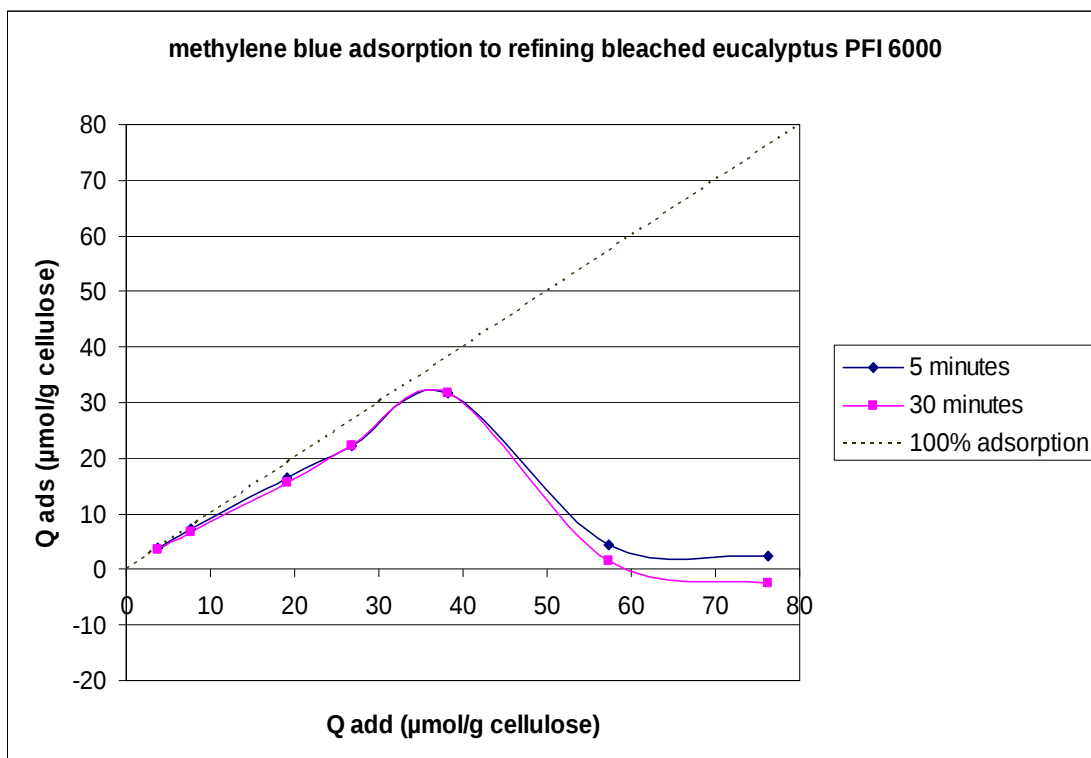


Figure 3.10 : methylene blue adsorption on to refinery bleached eucalyptus PFI 6000

It was surprisingly that the trend of sorption isotherms for bleached eucalyptus PFI 6000, Figure 3.10, are different from that of unbeaten and beaten PFI 3000 bleached pulp. The sorption is reduced rapidly when increasing the concentration of methylene blue. The same desorption appearance can be occurred.

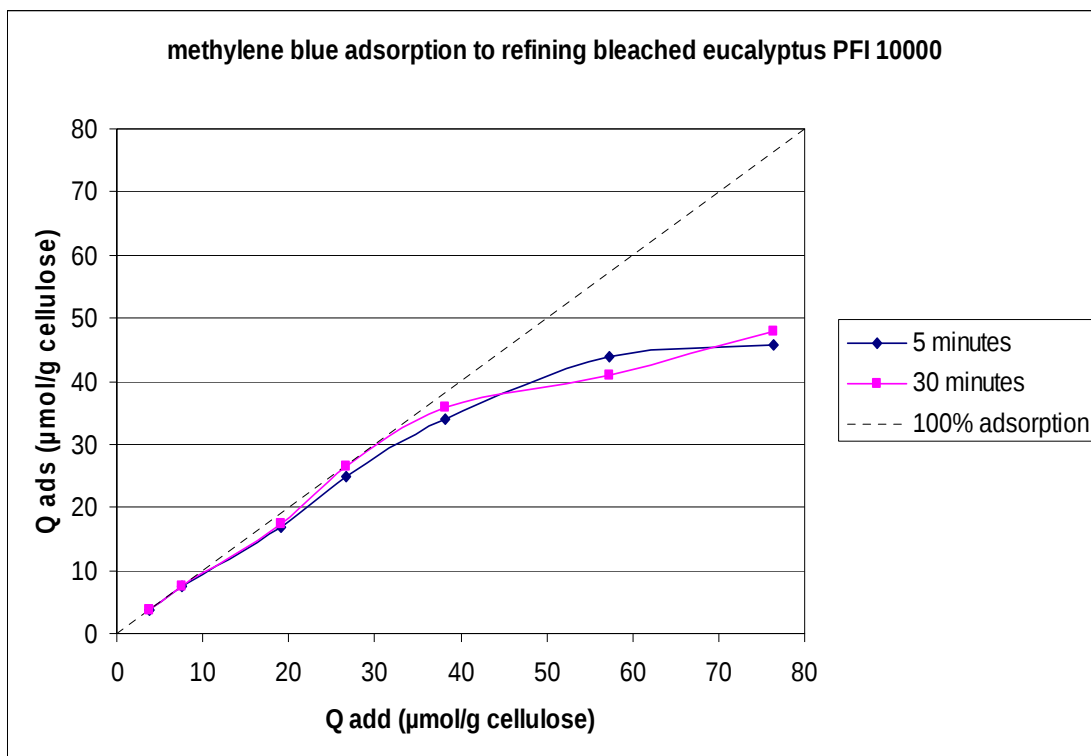


Figure 3.11 : methylene blue adsorption on to refinery bleached eucalyptus PFI 10000

It is found that the methylene blue sorption isotherm of bleached eucalyptus PFI 10000 during 5 and 30 minutes are very close. Moreover, it is obviously that increasing the concentration, increase the sorption. As the lower concentration such 2C and 5C, the sorptions are closely complete and this shows linearity curve in this range. Desorption can be occurred in higher concentration.

The comparative of methylene blue adsorption on to different degrees of refinery bleached eucalyptus during 30 minutes is presented in Figure 3.12 and the correspondence data is shown in Table 3.6.

Table 3.6 : methylene blue sorption for unbeaten and beaten bleached eucalyptus during 30 minutes.

Type of pulp	Concentration of methylene blue (M)	Q add ($\mu\text{mol/g}$ cellulose)	Q ads ($\mu\text{mol/g}$ cellulose)	% adsorption
Bleached eucalyptus (non refinery)	2C	7.64	7.45	97.53
	5C	19.09	18.90	98.98
	7C	26.71	26.32	98.54
	10C	38.15	34.79	91.19
	15C	57.23	41.74	72.92
	20C	76.31	45.84	60.07
Bleached eucalyptus (PFI 3000)	2C	7.63	7.44	97.42
	5C	19.08	15.62	81.88
	7C	26.71	19.94	74.64
	10C	38.16	21.70	56.87
	15C	57.23	27.72	48.44
	20C	76.31	23.40	30.67
Bleached eucalyptus (PFI 6000)	2C	7.64	6.81	89.11
	5C	19.10	15.68	82.09
	7C	26.71	19.94	74.64
	10C	38.20	31.85	83.38
	15C	57.23	1.62	2.83
	20C	76.31	-2.53	-3.31
Bleached eucalyptus (PFI 10000)	2C	7.64	7.46	97.69
	5C	19.10	17.31	90.65
	7C	26.71	26.39	98.82
	10C	38.15	35.97	94.28
	15C	57.23	40.99	71.63
	20C	76.31	47.94	62.82

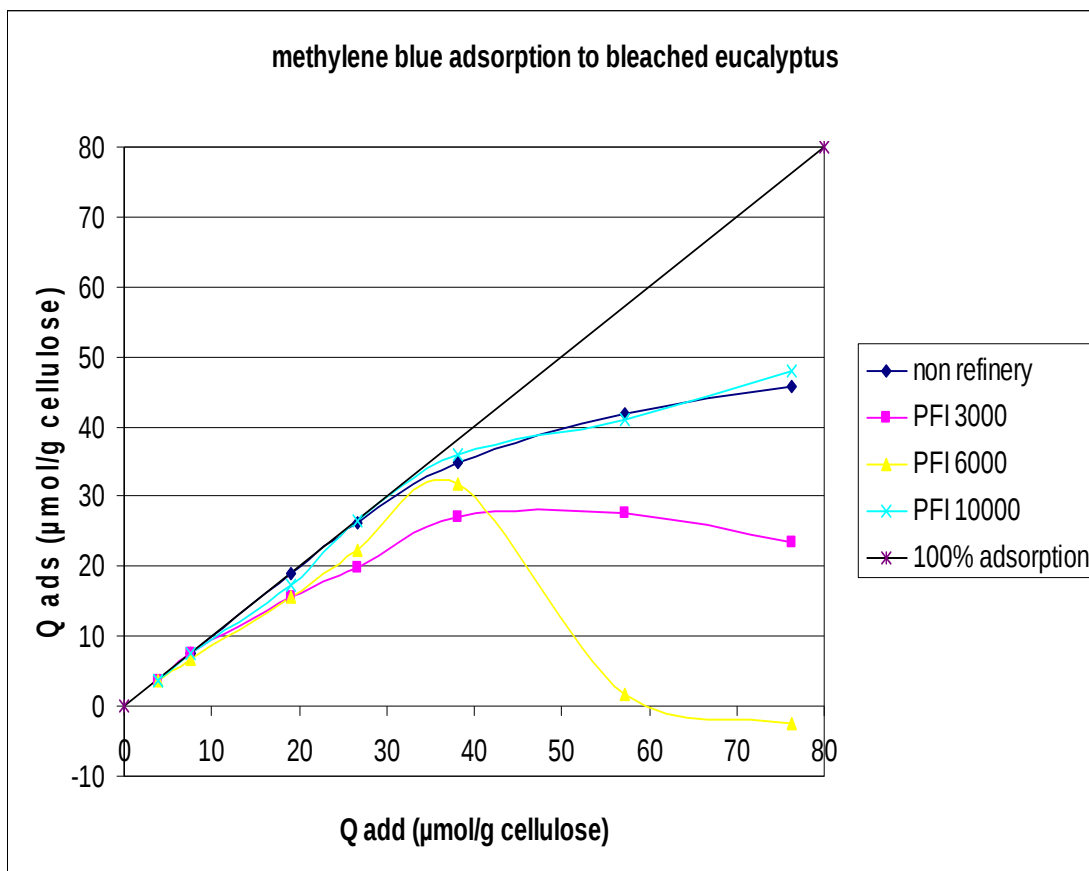


Figure 3.12 : Comparison of methylene blue adsorption on to bleached eucalyptus at different degrees of beating : 30 minutes

For lower concentration of methylene blue, we obvious from Figure 3.12 that the degree of beating does not effect to bleached eucalyptus and have complete adsorption. With higher concentration, the desorption can be occurred, and the degree of beating effect to the sorption. We cannot now explain why the sorption to non refinery and refinery PFI 10000 are very close and have the same curve during the reaction time at any beginning concentration of dye. At present we cannot explain many much about this, we maybe change the relation of curve to Langmuire model as previously expected.

The other results of softwood of Tarascon which concern the present thesis work are shown in Figure 3.13-3.15 and the comparative effect of degree of beating pulps are presented in Figure 3.16.

Softwood of Tarascon in buffer system

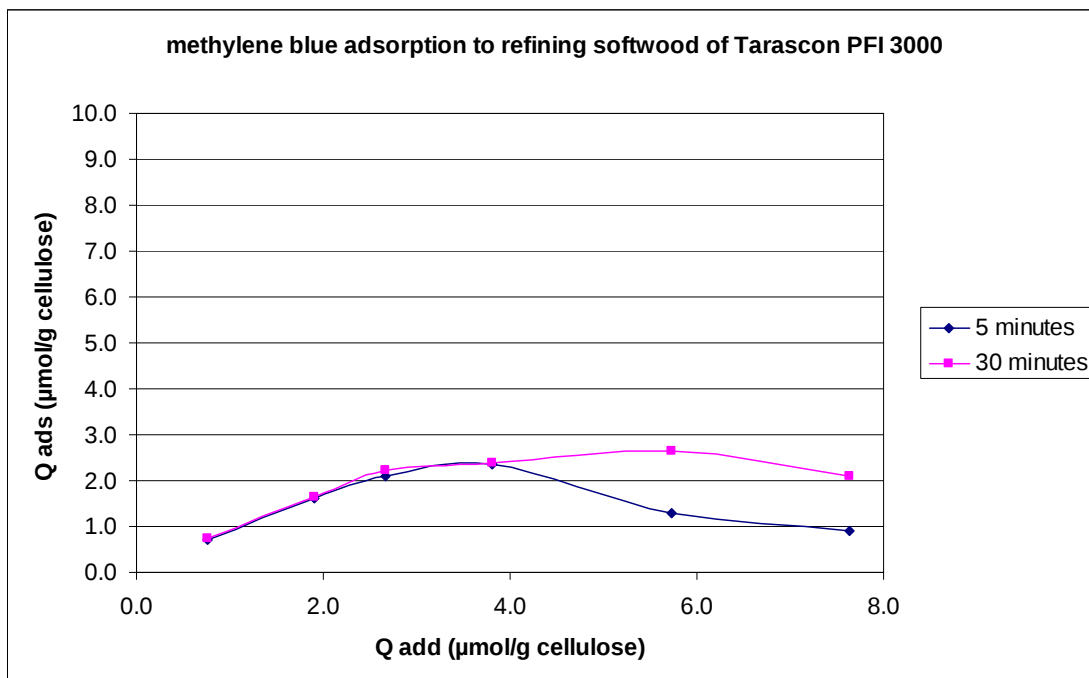


Figure 3.13 : methylene blue adsorption on to refining softwood of Tarascon PFI 3000

Consider to the methylene blue sorption to refinery softwood of Tarascon PFI 3000 during 5 and 30 minutes, it indicates that the sorption is stable for low concentration such 2C, 5C, 7C and 10C and completed adsorption for 2C. Comparison between the adsorption curve during 5 and 30 minutes, we found that increasing concentration of methylene blue such 15C and 20C, the sorption during 30 minutes is higher than that of 5 minutes. We suggest that the desorption of methylene blue maybe occurred in the case of very high concentration during 30 minutes, however, it is difficult to say for the curve during 5 minutes.

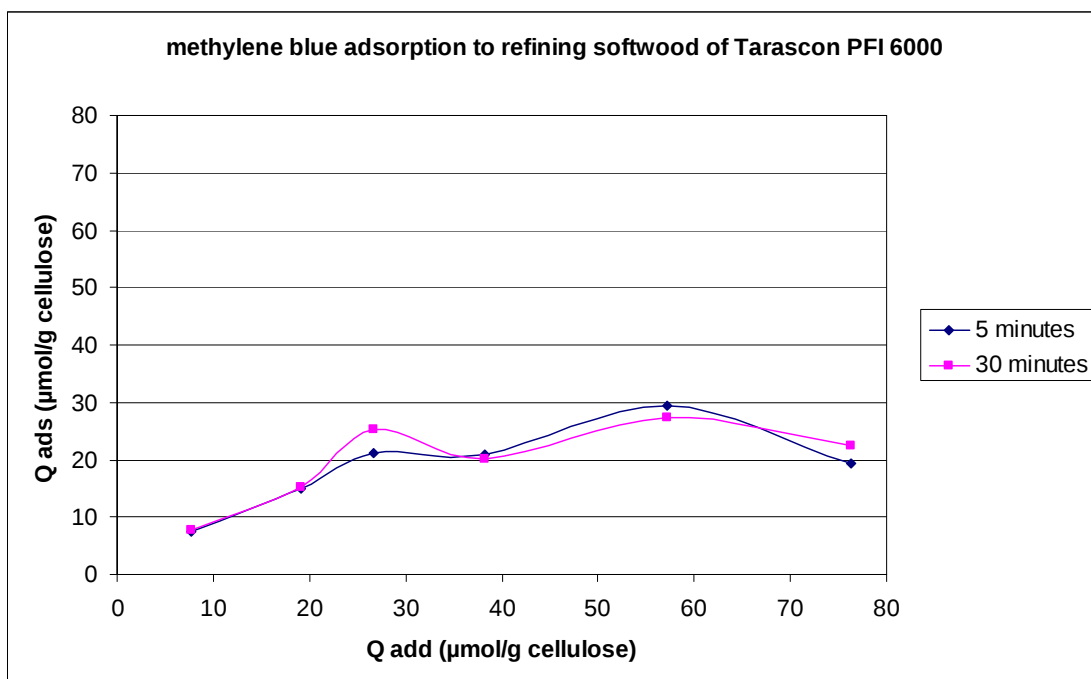


Figure 3.14 : methylene blue adsorption on to refining softwood of Tarascon PFI 6000

Obviously that the sorption curve of refinery softwood of Tarascon PFI 3000 at 5 and 30 minutes are very close for any concentration of methylene blue and we cannot describe further more.

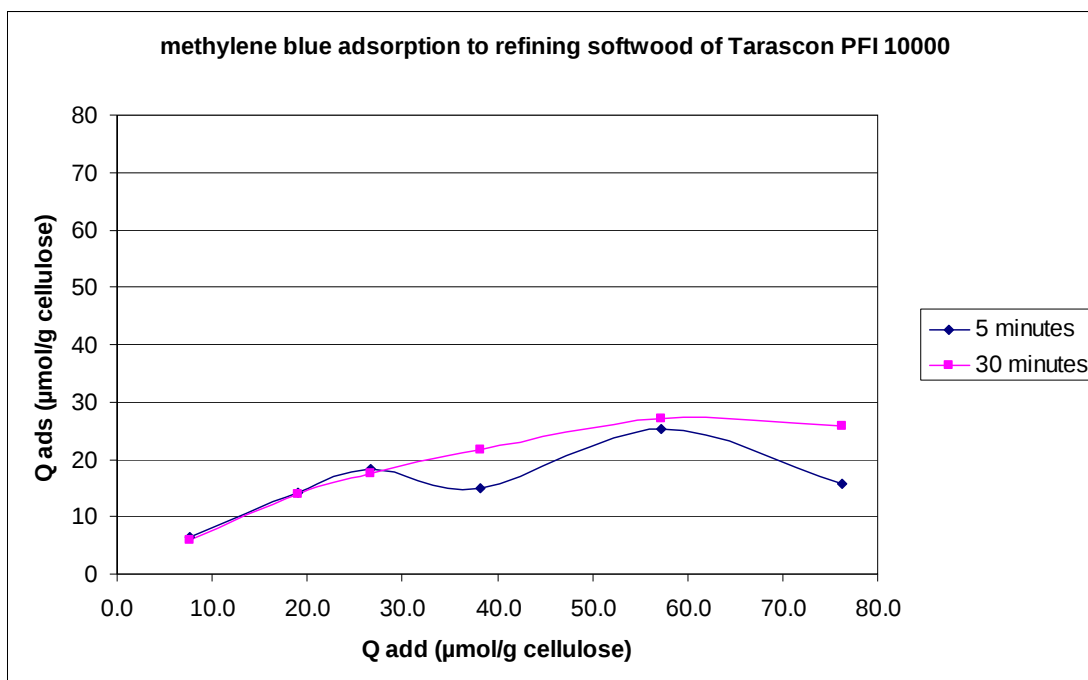


Figure 3.15 : methylene blue adsorption on to refining softwood of Tarascon PFI 10000

For the higher degree of beating softwood of Tarascon, PFI 10000, Figure 3.15 shows the sorption for very low concentration of methylene blue during 5 and 30 minutes were very close, 2C, 5C and 7C.

The methylene blue adsorption to different degrees of beating softwood of Tarascon during 30 minutes are written in Table 3.13 and the comparison sorption isotherms, hence, are plotted in Figure 3.16.

Table 3.7 : methylene blue sorption for unbeaten and beaten softwood of Tarascon during 30 minutes.

Type of pulp	Concentration of methylene blue (M)	Q add ($\mu\text{mol/g}$ cellulose)	Q ads ($\mu\text{mol/g}$ cellulose)	% adsorption
Softwood of Tarascon (PFI 3000)	2C	7.63	7.45	97.62
	5C	19.08	16.48	86.36
	7C	26.71	22.36	83.72
	10C	38.16	24.02	62.94
	15C	57.24	26.42	46.16
	20C	76.32	21.05	27.59
Softwood of Tarascon (PFI 6000)	2C	7.63	7.65	100.21
	5C	19.08	15.13	79.32
	7C	26.71	25.32	94.77
	10C	38.16	20.22	52.98
	15C	57.24	26.42	46.16
	20C	76.32	22.36	29.30
Softwood of Tarascon (PFI 10000)	2C	7.63	5.82	76.23
	5C	19.08	13.89	72.82
	7C	26.71	17.54	65.68
	10C	38.16	21.70	56.87
	15C	57.24	27.12	47.38
	20C	76.32	25.86	33.88

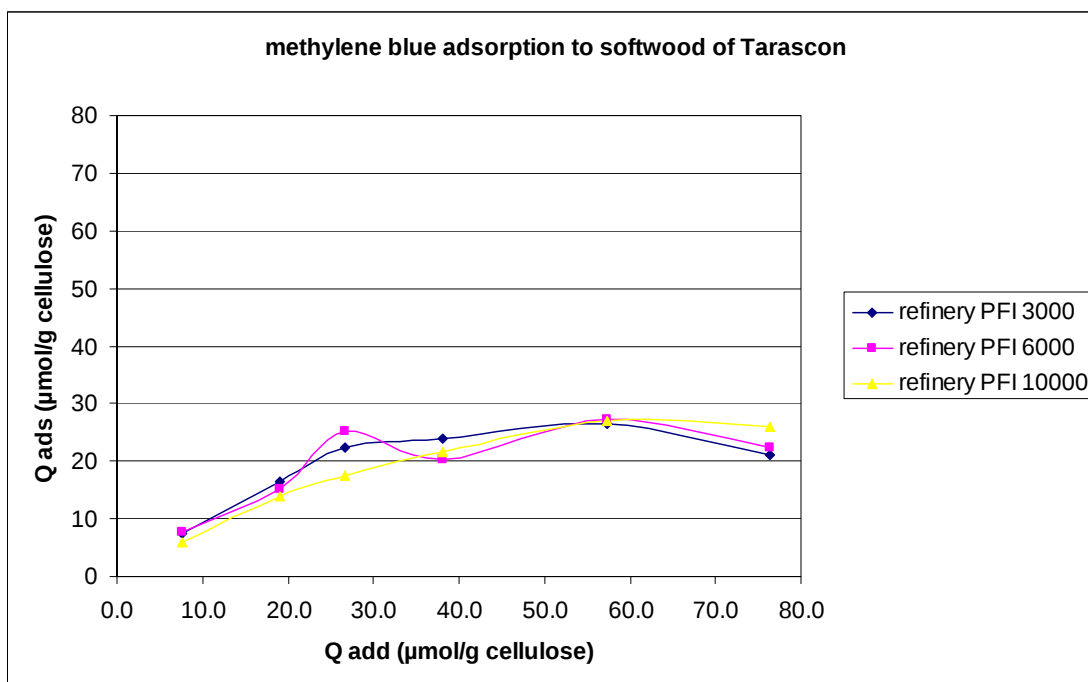


Figure 3.16 : Comparison of methylene blue adsorption on to softwood of Tarascon at different degrees of beating : 30 minutes

Considering the comparison of methylene blue sorption on to different degrees of beating softwood of Tarascon, Figure 3.16, we observed their sorption value for any beating, i.e., PFI 3000, 6000 and 10000 are similar at very low and high concentration except for the concentration of 5C that more different value than the other points of results. We cannot describe any more this appearance.

The other type of type, linter cotton was chosen to do the experiment. From now on, we will present their sorption isotherms.

Linter cotton in buffer system

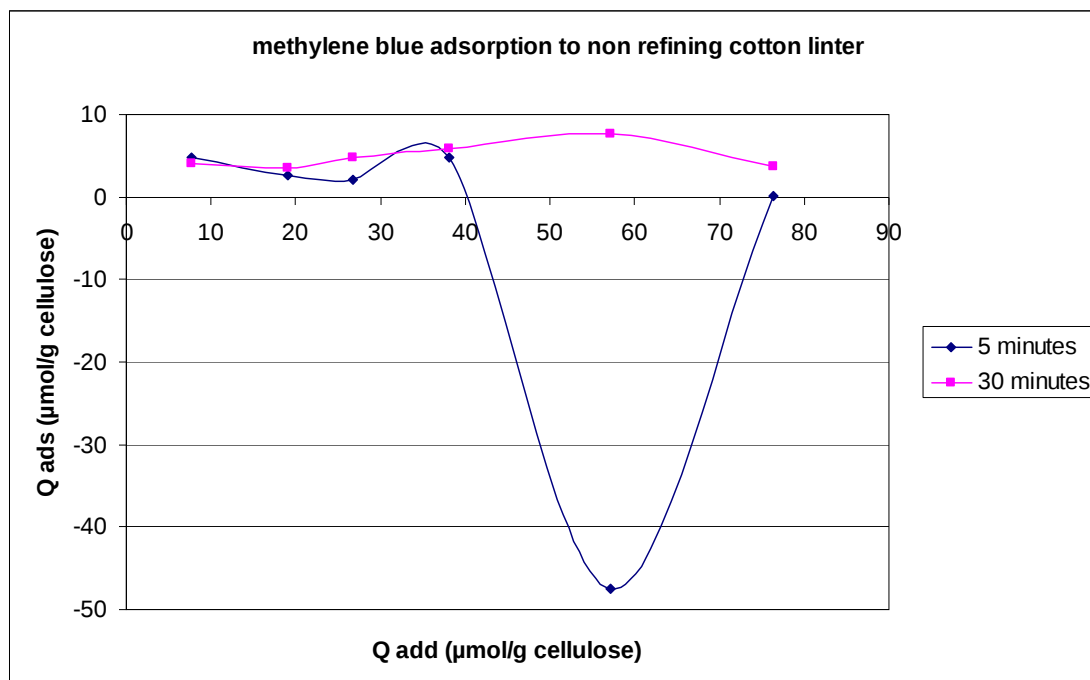


Figure 3.17 : methylene blue adsorption on to non refinery linter cotton

For unbeaten cotton linter, the sorption curve during 5 and 30 minutes are very close, just one point of data is much more different for 15C of dye concentration. There has no the clearly reason to prove about this behavior. We thought that the quantity of colloid from double filtrate for each experiment is not the same quantity, so this is may be the one reason to explain about this.

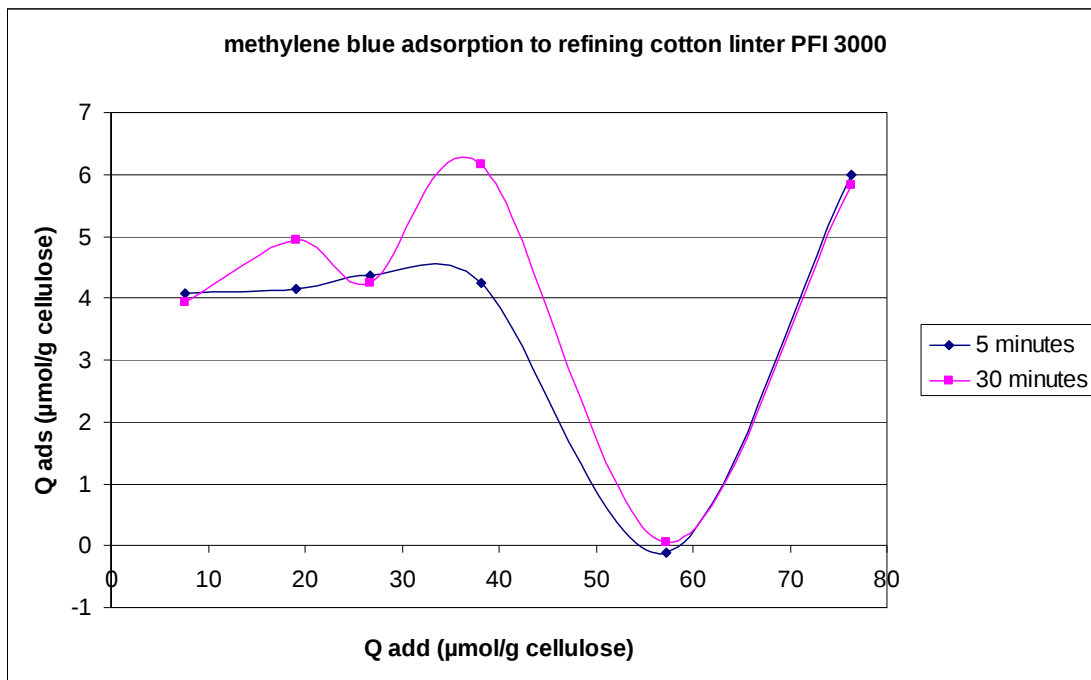


Figure 3.18 : methylene blue adsorption on to refining linter cotton PFI 3000

It is observed that sorption curve for beaten linter cotton, PFI 3000, during 5 and 30 minutes are very close. The sorption value for 15C of methylene blue concentration is much more different from the others.

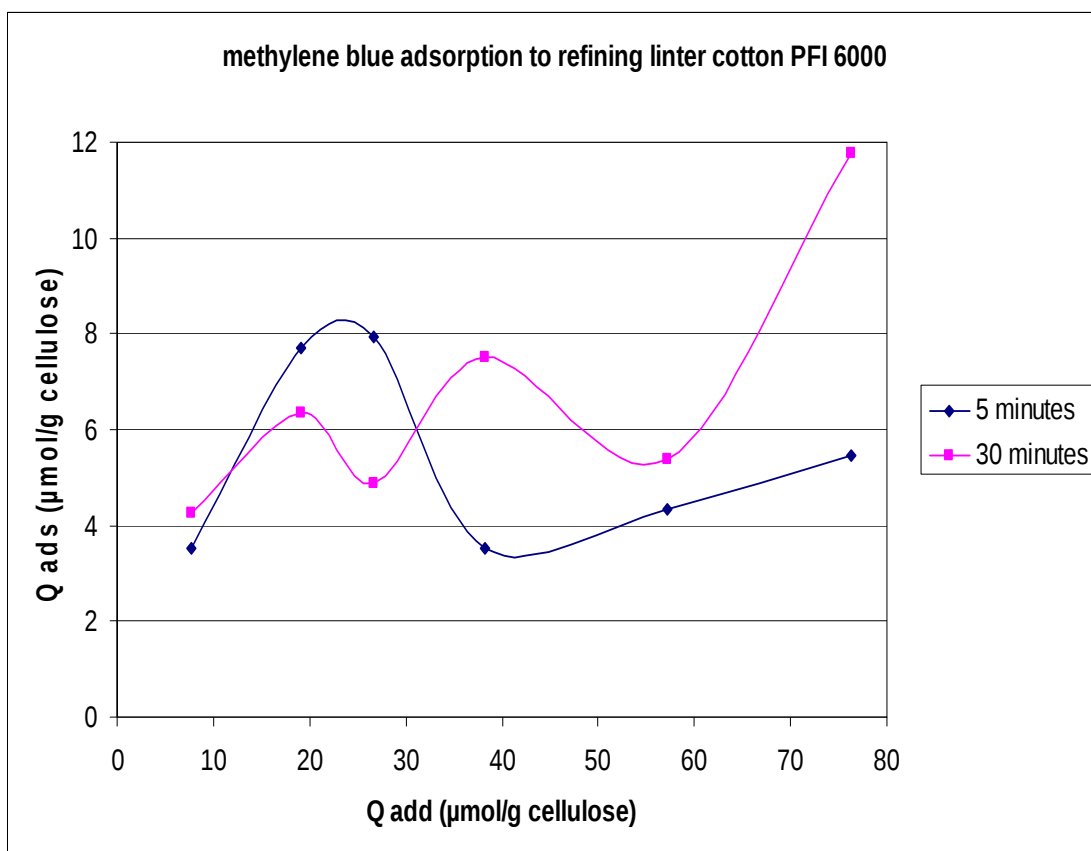


Figure 3.19 : methylene blue adsorption on to refining linter cotton PFI 6000

The sorption isotherm of linter cotton PFI 6000 during 5 and 30 minutes are presented in Figure 3.19. Obviously, we cannot show the normal form of equation to these curves.

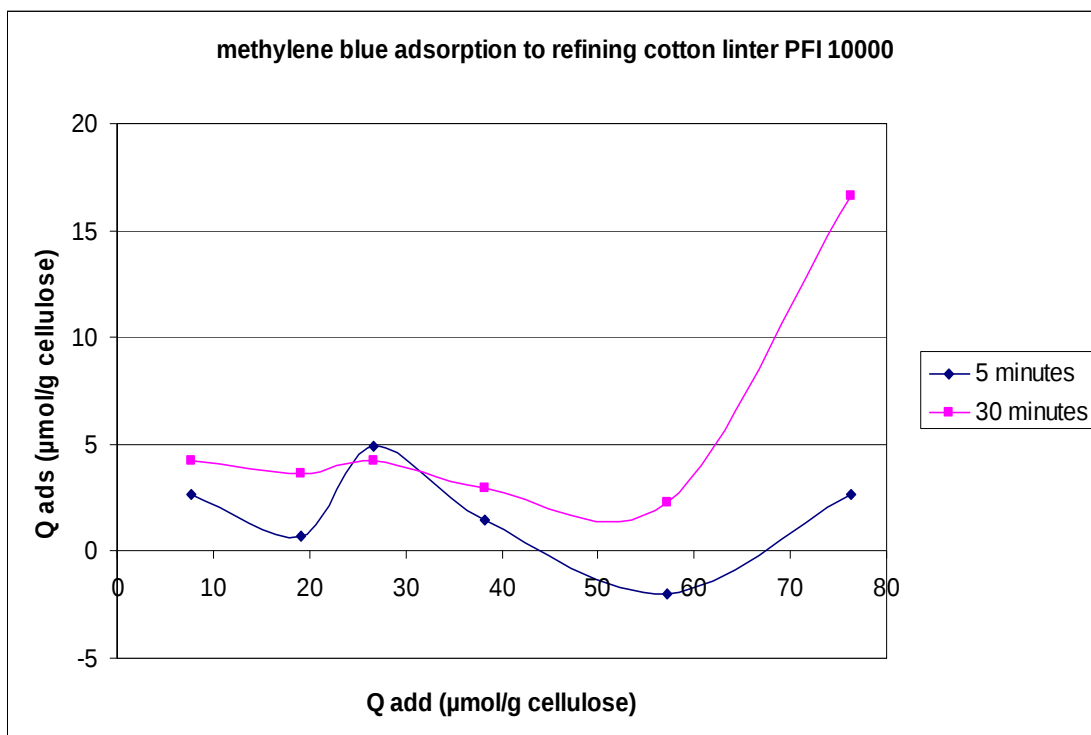


Figure 3.20 : methylene blue adsorption on to refining linter cotton PFI 10000

For beaten linter cotton PFI 10000, the sorption curve during 30 minutes is higher than the one of that of 5 minutes for every concentration of methylene blue except for the concentration of 7C.

Table 3.8 : methylene blue sorption for unbeaten and beaten linter cotton during 30 minutes.

Type of pulp	Concentration of methylene blue (M)	Q add ($\mu\text{mol/g}$ cellulose)	Q ads ($\mu\text{mol/g}$ cellulose)	% adsorption
Linter cotton (non refinery)	2C	7.63	4.14	54.24
	5C	19.08	3.55	18.63
	7C	26.71	4.75	17.79
	10C	38.15	5.85	15.34
	15C	38.15	5.85	15.34
	20C	76.31	3.76	4.92
Linter cotton (PFI 3000)	2C	7.63	3.93	51.50
	5C	19.08	4.94	25.88
	7C	26.72	4.23	15.85
	10C	38.16	6.17	16.16
	15C	57.25	0.06	7.27
	20C	76.36	5.82	7.62
Linter cotton (PFI 6000)	2C	7.63	4.25	55.63
	5C	19.08	6.34	33.21
	7C	26.72	4.90	18.31
	10C	38.18	7.49	19.62
	15C	57.25	5.39	9.42
	20C	76.36	11.75	15.39
Linter cotton (PFI 10000)	2C	7.63	4.26	55.85
	5C	19.08	3.66	19.19
	7C	26.72	4.24	15.86
	10C	38.16	2.93	7.68
	15C	57.26	2.25	3.93
	20C	76.32	16.60	25.86

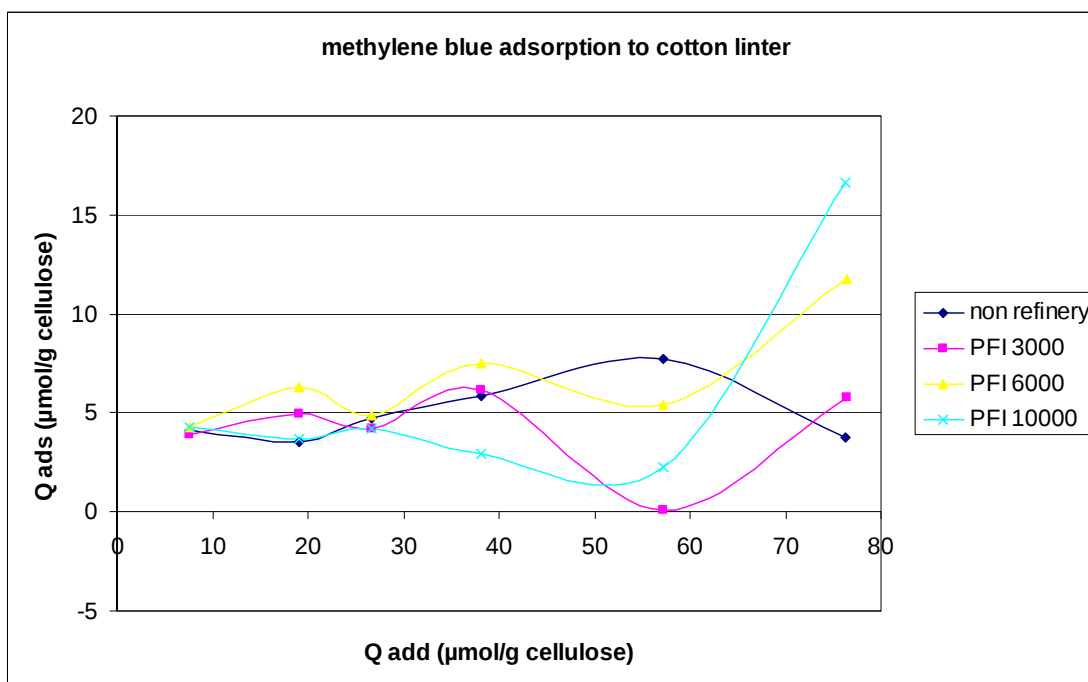


Figure 3.21 : Comparison of methylene blue adsorption on to linter cotton at different degrees of beating : 30 minutes

From these results, it is difficult to explain about the behavior of methylene blue adsorption. This is the reason why we decided to do the experiment of zeta potential to better understanding for this work. Other variables, i.e., diffusion, surface of fiber, the size of pore and porous volume maybe effect these results. The other idea is to try to change the adsorption isotherm of methylene blue to the model of Langmuire equation. The other worker [18,23] support this equation. There are not many research about methylene blue sorption to fiber pulps, hence, we applied from the other research of other topic of dye sorption to activated carbon, soil, etc. to support this idea such the worker [25]. According to the worker [26] studied the dye binding capacity of adsorbents produced from waste water sludge. Adsorption equilibrium of methylene blue by these materials was described in terms both of Langmuir and Freundlich equations. Rubin. E et al [27] was studied for removal of methylene blue from aqueous solutions using biosorbent. From their results, the equilibrium binding has been described in terms of Langmuir and Freundlich

isotherms. This is the first time to propose the model of methylene blue on to cellulosic pulps (suspension fiber of pulps, homogenous system).

3.3 Zeta potential

3.3.1. Initial pulps

As mentioned in the used conditions to measure the zeta potential were optimised by Missaoui [9]. From his work, in the suspension of cellulose, two types of polyelectrolyte, poly(DADMAC) and starch were used for this method. The different concentrations of total electrolyte were studied for his work. And it is found that the results of poly(DADMAC) is better because of its capability of charge, then this is the reason why we choose poly(DADMAC) as cationic polyelectrolyte for our work. Furthermore, we found that the preliminary results of our work with measurement zeta potential of the double filtrate of suspension of cellulose pulp did not work, this may be due to less capability of charge. This is the other reason to contribute to decide to use poly(DADMAC) as a polyelectrolyte.

Particularly, the electrical conductivity of the suspensions, which plays an important role since screening phenomena could take place and affect significantly the zeta potential values. Dilute concentration of salt solutions were used to reduce the specific viscosity in the solution which give in good result even though for the work of Missaoui [9]. In our research, a 0.1M NaCl solution was added in order to maintain the electrical conductivity of the suspensions at the values i.e., range values between 450 and 660 $\mu\text{S/cm}$.

The zeta-potential of the initial pulps was determined and shown that bleaching eucalyptus pulps have the highest anionic sites content. Given the experimental error related to zeta potential measurements ($\pm 2\text{-}3$ mV), it can be concluded that different levels of beating did not induce a significant effect to this parameter. Softwood pulps behaved similarly, although with a lower intrinsic anionic character, as expected from their lower content in hemicelluloses. It is found that linter cotton shows an intermediate behaviour, which is in agreement with Fengel and

Wegener [28] ; Fisher and Heinze [29], Gullichsen and Paulapuro [30]; Kennedy et al. [31]).

Table 3.9 : Zeta potential of different pulps at various degree of beating.

Degree of beating	Zeta potential (mV)		
	Bleached eucalyptus	Softwood of Tarascon	Lintier cotton
0	-27.60	-17.3	-20.6
3000	-27.40	-17.9	-18.5
6000	-24.20	-17.6	-16.8
10000	-24.20	-17.7	-14.8

3.3.2. Evolution of zeta potential with poly(DADMAC) addition

3.3.2.1. Bleached eucalyptus

The zeta potential of bleached eucalyptus was measured at different of the addition of quantity of the polyelectrolyte (**PE**), the poly(DADMAC) in our case, as illustrated in Figures 3.22 to 3.26, which show that the increasing of the added poly(DADMAC) increased the values of the zeta potential for unbeaten and various beaten pulps investigated. Moreover, the total poly(DADMAC), necessary to neutralise the electrical charge (isoelectric point) at the surface of the fibres increased with increasing beating level. This can attribute to the higher specific surface area of the pulps after refining.

Non refined bleached eucalyptus pulps required 0.036% (w/w with respect to o.d. pulps) of poly(DADMAC) to reach the isoelectric point, as summarized in Table 3.10. Such a quantity corresponds to cationic demand of 2.2 $\mu\text{eq/g}$ of cellulose. For refined pulps at 3000, 6000 and 10000 revolutions, the total added poly(DADMAC)

necessary to neutralise the cellulose surface electrical charges are 0.12, 0.19 and 0.36%, respectively, which related to cationic demand of 7.4, 11.8 and 17.0 $\mu\text{eq/g}$ of cellulose, respectively. Thus, the value of cationic demands increased more than 3 and 5 times, for bleached eucalyptus PFI 3000 and 6000, respectively, and practically 8 times, for bleached eucalyptus PFI 10000. This significant increase is probably due to the effect of mechanical action associated to refining of the fibres in aqueous medium, which develops the surface area of the pulps, thus inducing a higher demand on polycation macromolecules.

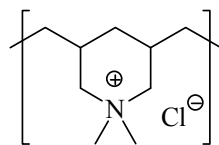
The cationic demand was calculated from the following expression:

$$\text{Cationic demand (meq/100g of cellulose)} = M_{\text{poly(DADMAC)}} \text{ (g/100g of cellulose)} \times 6.192 \text{ (meq/g of Poly(DADMAC))} \dots 1$$

where:

- $M_{\text{poly(DADMAC)}}$ is the weight of poly(DADMAC) needed to reach the isoelectric point when titrating 100 g of cellulose.

- 6.192 is the number of meq per g of poly(DADMAC), obtained by dividing the number of cationic groups (quaternary ammonium) by the mass of the repeating poly(DADMAC) unit, i.e. $\frac{1}{161.5}$ (see the chemical structure below). In fact, as seen from the structure illustrated below, the repeating unit of poly(DADMAC) is $\text{C}_8\text{H}_{16}\text{NCl}$.



Poly(DADMAC) (PE)

$$\text{Cationic demand (}\mu\text{eq/g cellulose)} = \text{equation 1} \times 10 \dots\dots\dots 2$$

Table 3.10 : Cationic demand of bleached eucalyptus at different degrees of beating

Bleached eucalyptus	poly(DADMAC) (% w/w)	Cationic demand ($\mu\text{eq/g}$ of cellulose)
Non refinery	0.036	2.2
PFI 3000	0.12	7.4
PFI 6000	0.19	11.8
PFI 10000	0.275	17.0

Table 3.11 : Zeta potential of added Poly(DADMAC) for unbeaten bleached eucalyptus

Total Poly(DADMAC)		Results	
concentration (%)	V added (ml)	Zeta potential (mV)	Conductivity (mS)
0	0	-27.60	0.523
0.05	0.5	-19.90	0.517
0.10	1.0	-8.80	0.477
0.15	1.5	-2.80	0.510
0.20	2.0	4.40	0.539
0.25	2.5	7.10	0.516
0.30	3.0	14.20	0.530

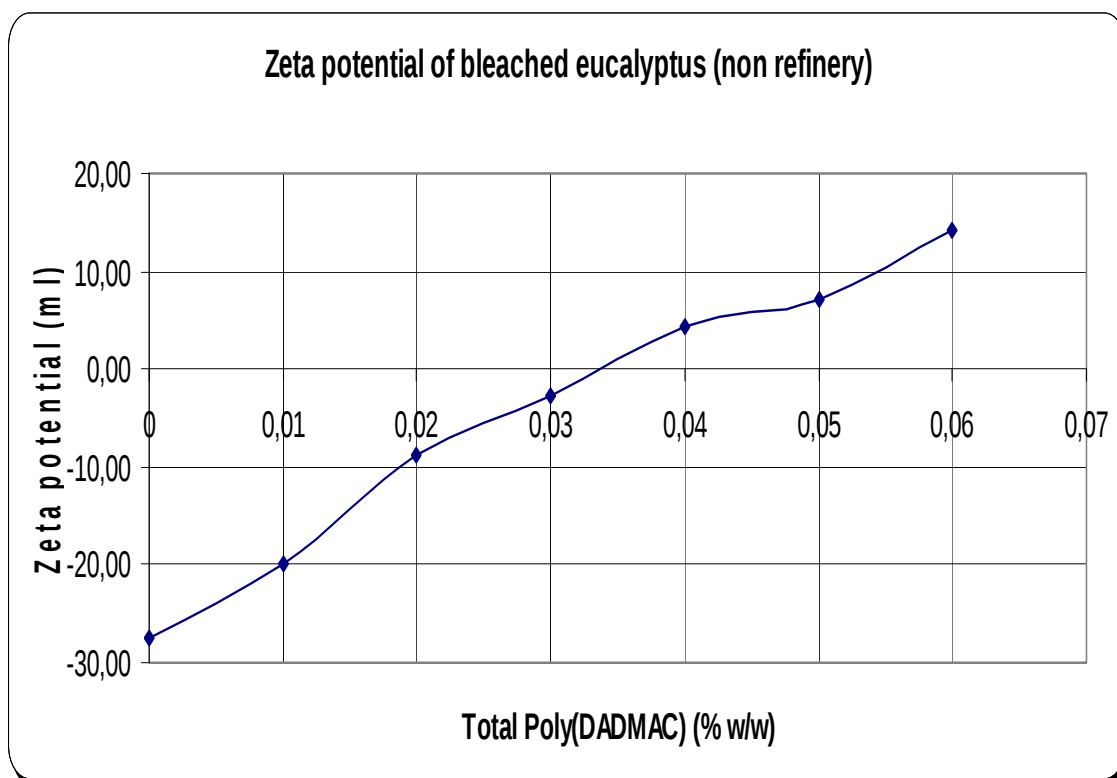


Figure 3.22 : Zeta potential of unbeaten bleached eucalyptus

Table 3.12 : Zeta potential of added Poly(DADMAC) for refinery bleached eucalyptus PFI 3000

Total Poly(DADMAC)		Results	
concentration (%)	V added (ml)	Zeta potential (mV)	Conductivity (mS)
0	0	-27.60	0.523
0.01	0.5	-19.90	0.517
0.02	1.0	-8.80	0.477
0.03	1.5	-2.80	0.510
0.04	2.0	4.40	0.539
0.05	2.5	7.10	0.516
0.06	3.0	14.20	0.530

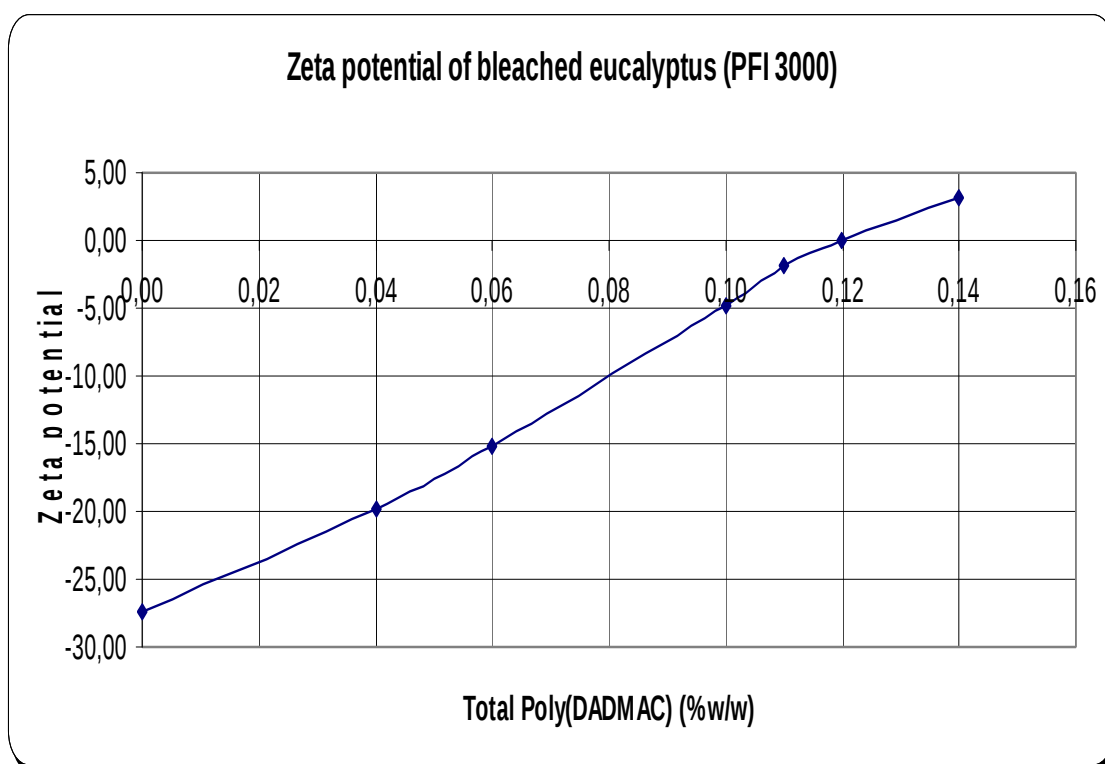


Figure 3.23 : Zeta potential of bleached eucalyptus PFI 3000

Table 3.13 : Zeta potential of added Poly(DADMAC) for refinery bleached eucalyptus PFI 6000

Total Poly(DADMAC)		Results	
concentration (%)	V added (ml)	Zeta potential (mV)	Conductivity (mS)
0.00	0.0	-24.20	0.609
0.06	3.0	-18.90	0.393
0.10	5.0	-13.40	0.621
0.14	7.0	-7.30	0.556
0.16	8.0	-3.90	0.515
0.18	9.0	-2.50	0.511
0.20	10.0	1.60	0.600

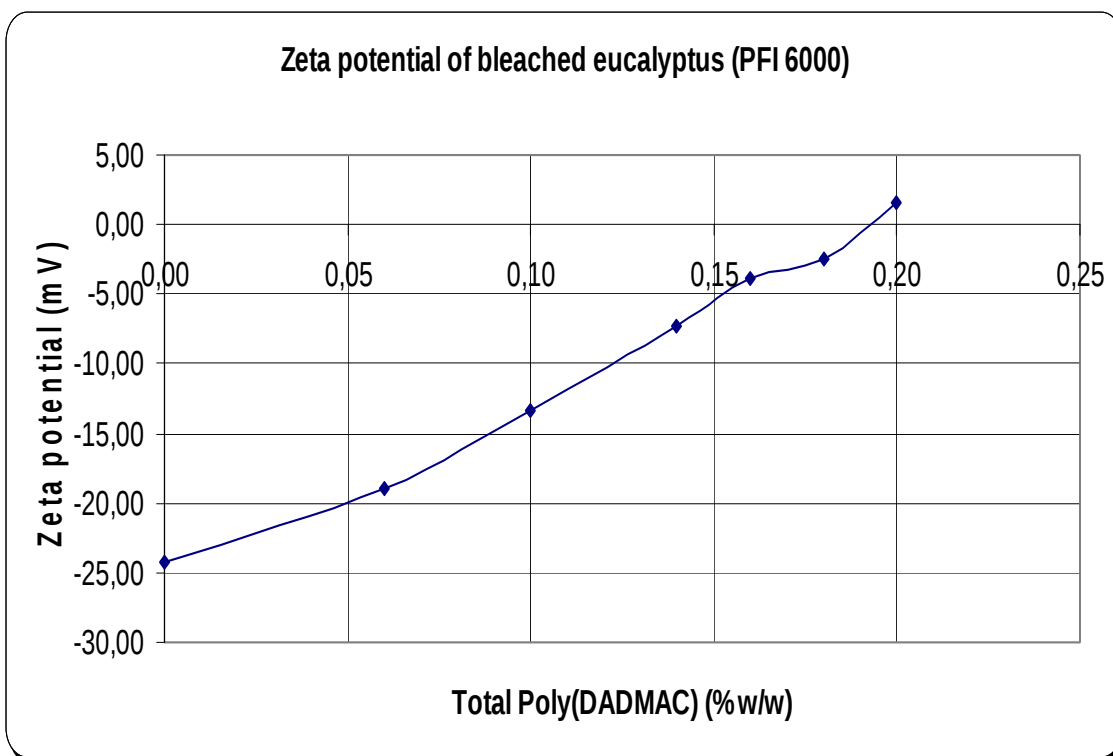


Figure 3.24 : Zeta potential of bleached eucalyptus PFI 6000

Table 3.14 : Zeta potential of added Poly(DADMAC) for refinery bleached eucalyptus PFI 10000

Total Poly(DADMAC)		Results	
concentration (%)	V added (ml)	Zeta potential (mV)	Conductivity (mS)
0.00	0	-24.20	0.548
0.10	5	-17.40	0.545
0.16	8	-10.90	0.544
0.20	10	-7.30	0.54
0.24	12	-3.30	0.539
0.30	15	1.90	0.558
0.34	17	4.30	0.526

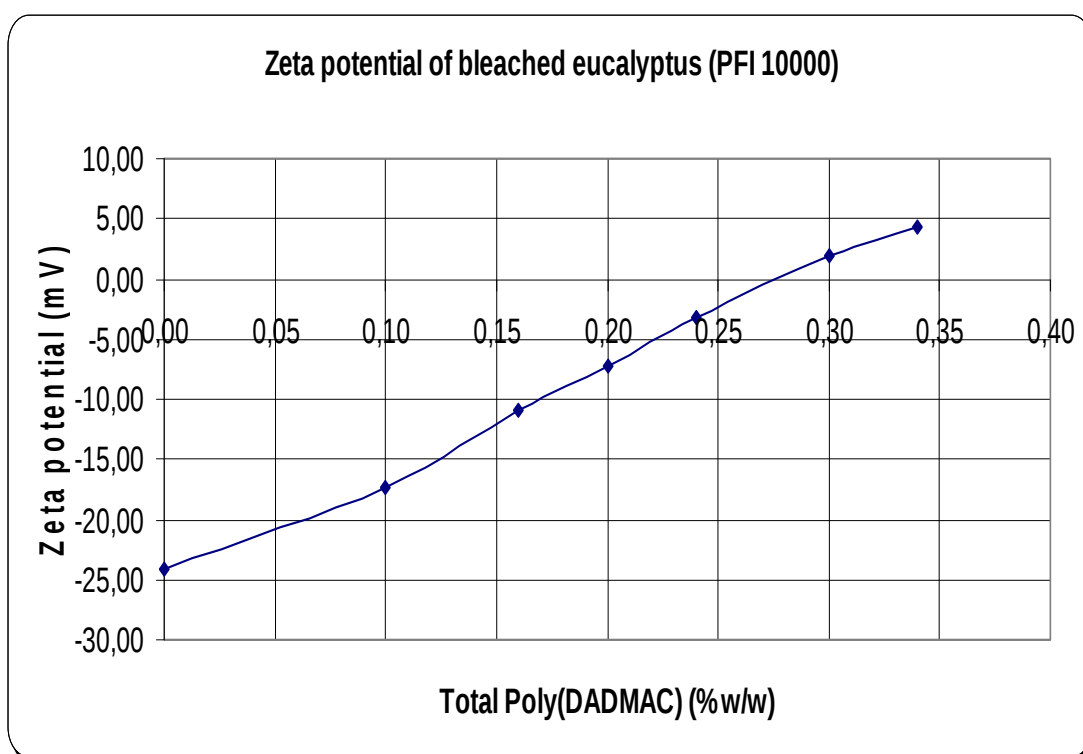


Figure 3.25 : Zeta potential of bleached eucalyptus PFI 10000

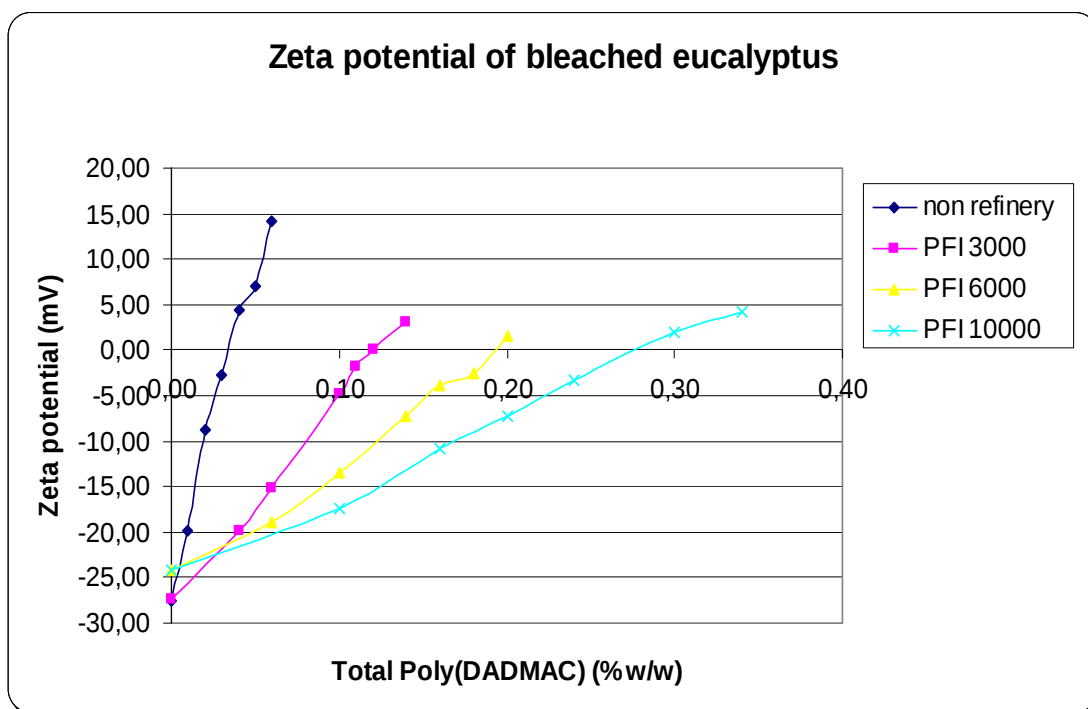


Figure 3.26 : Comparison of zeta potential of bleached eucalyptus.

3.3.2.2. Softwood of Tarascon

Figures 3.27-3.31 illustrate the evolution of the zeta potential of the softwood of Tarascon at different concentration of poly(DADMAC). As in the case of bleached eucalyptus pulps, the increase of degree of beating increases the amount of the added poly(DADMAC). Consequently, the values of the zeta potential of different levels of refinery pulps were investigated increased with refining intensity. In fact, concentration of poly(DADMAC), necessary to reach the isoelectric point of the fibres increased with increasing beating level, as summarizes Table 3.15, which collects the data related to this set of experiments.

Unbeaten softwood of Tarascon pulps required much less concentration to be neutralized compared with bleached eucalyptus, i.e., 0.01% (w/w with respect to o.d. pulps) of poly(DADMAC). This value related to cationic demand of 0.6 $\mu\text{eq/g}$ of cellulose (3.7 times less than bleached eucalyptus pulps). Refining of pulps at 3000, 6000 and 10000 revolutions, induced an increase of the poly(DADMAC) necessary to reach the isoelectric point of cellulose electrical charges, 0.06, 0.08 and 0.12%, respectively. Injecting these values to the Equation 1 yields cationic demand which related to anionic content of 3.6, 4.8 and 7.4 $\mu\text{eq/g}$ of cellulose, respectively. Here also, the anionic groups content increased by 6, 8 and more than 12 times, for bleached softwood of Tarascon PFI 3000, 6000 and 10000, respectively. This significant increase is probably due to the same reasons for bleached eucalyptus. These data are in agreement with those reported in the literature for similar species (Fisher and Heinze, [29], Gullichsen and Paulapuro, [30]; Kennedy et al. [31]).

Table 3.15 : Cationic demand of softwood of Tarascon at different degrees of beating.

Softwood of Tarascon	poly(DADMAC) (% w/w)	Cationic demand ($\mu\text{eq/g}$ of cellulose)
Non refinery	0.02	0.6
PFI 3000	0.06	3.7
PFI 6000	0.08	4.9
PFI 10000	0.12	7.4

Table 3.16 : Zeta potential of added Poly(DADMAC) for unbeaten softwood of Tarascon

Total Poly(DADMAC)		Results	
concentration (%)	V added (ml)	Zeta potential (mV)	Conductivity (mS)
0.00	0	-17.30	0.430
0.00	0.2	-9.70	0.425
0.01	0.4	-2.90	0.427
0.01	0.6	1.00	0.427
0.02	1.0	3.60	0.425
0.04	2.0	22.10	0.439
0.06	3.0	39.60	0.431

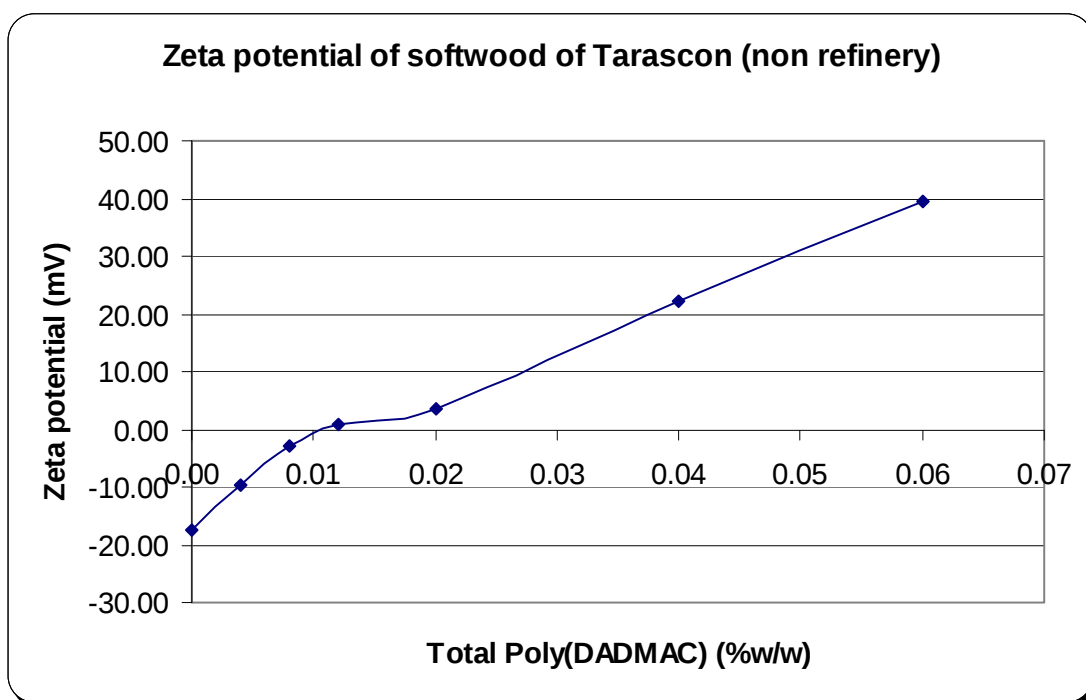


Figure 3.27 : Zeta potential of softwood of Tarascon (non refinery)

Table 3.17 : Zeta potential of added Poly(DADMAC) for refinery softwood of Tarascon PFI 3000

Total Poly(DADMAC)		Results	
concentration (%)	V added (ml)	Zeta potential (mV)	Conductivity (mS)
0.00	0	-17.90	0.614
0.01	0.5	-10.60	0.620
0.02	1.2	-7.30	0.630
0.03	1.7	-4.90	0.640
0.05	2.3	-2.50	0.660
0.06	3.0	0.00	0.650
0.07	3.6	1.80	0.650

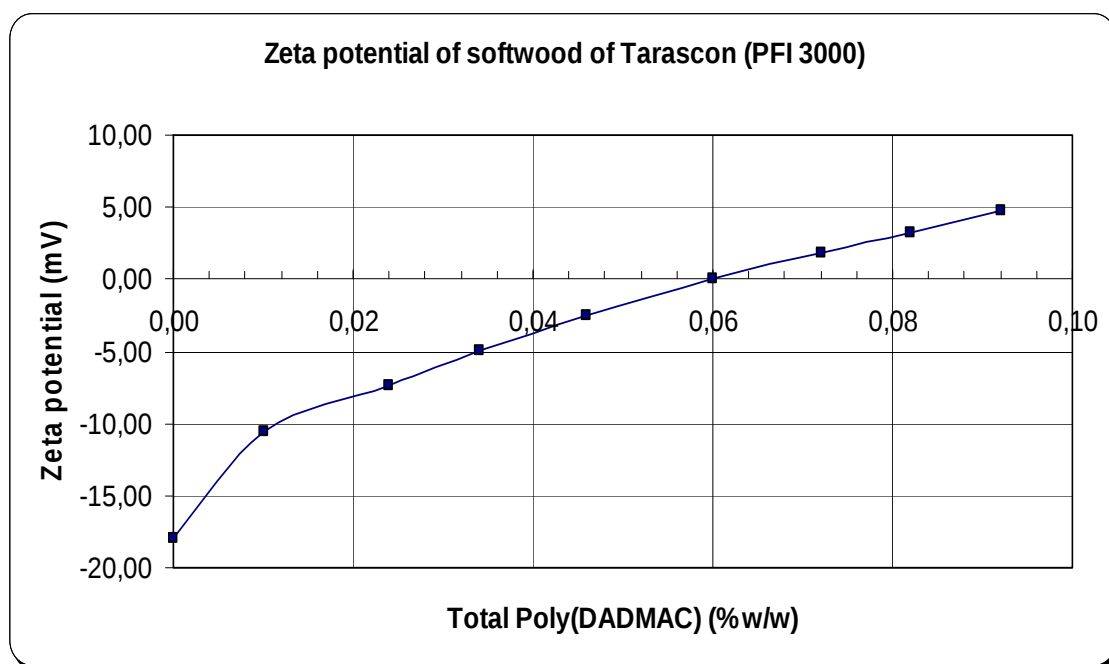


Figure 3.28 : Zeta potential of softwood of Tarascon PFI 3000

Table 3.18 : Zeta potential of added Poly(DADMAC) for refinery softwood of Tarascon PFI 6000

Total Poly(DADMAC)		Results	
concentration (%)	V added (ml)	Zeta potential (mV)	Conductivity (mS)
0.00	0	-17.60	0.535
0.01	0.5	-14.20	0.535
0.03	1.7	-9.60	0.546
0.05	2.3	-6.70	0.538
0.07	3.6	-3.70	0.543
0.08	4.1	1.30	0.202
0.09	4.6	2.80	0.166

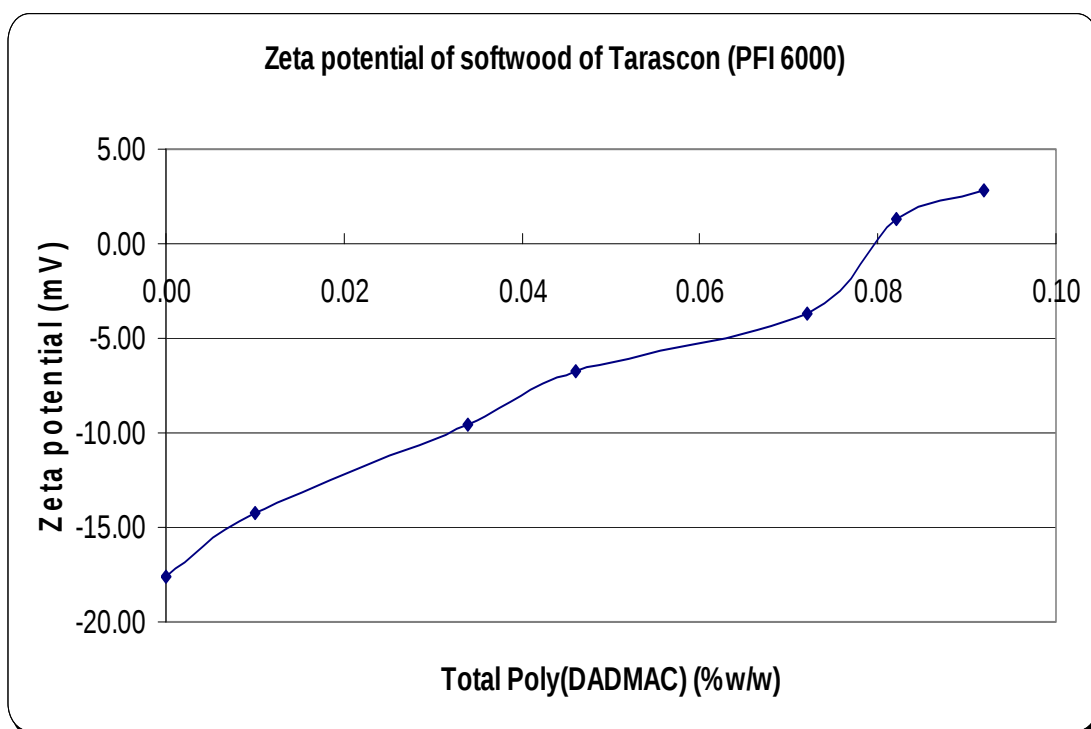


Figure 3.29 : Zeta potential of softwood of Tarascon PFI 6000

Table 3.19 : Zeta potential of added Poly(DADMAC) for refinery softwood of Tarascon PFI 10000

Total Poly(DADMAC)		Results	
concentration (%)	V added (ml)	Zeta potential (mV)	Conductivity (mS)
0.00	0	-17.70	0.565
0.01	0.5	-15.00	0.571
0.03	1.7	-11.50	0.597
0.06	3.0	-7.80	0.591
0.07	3.6	-6.00	0.606
0.09	4.6	-3.60	0.554
0.11	5.6	-1.30	0.554
0.12	6.0	0	0.604
0.13	6.6	0	0.601
0.14	7.0	0.9	0.559

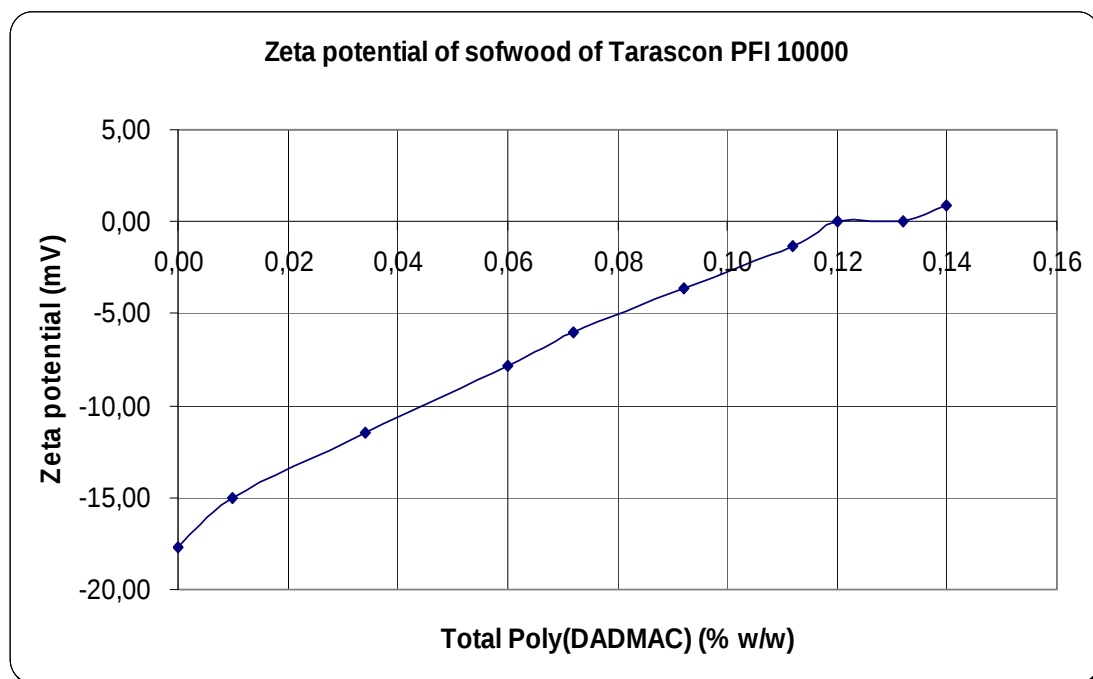


Figure 3.30 : Zeta potential of softwood of Tarascon PFI 10000

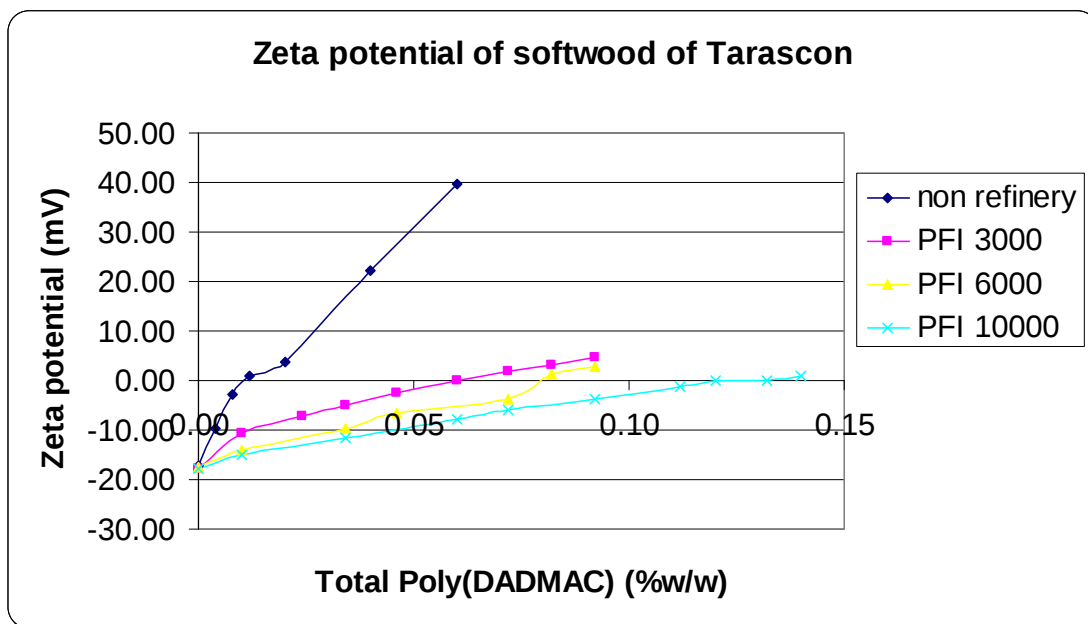


Figure 3.31 : Comparison of zeta potential of softwood of Tarascon at different degrees of beating

3.3.2.3. Cotton linters pulps

Figures 3.31-3.35 show the zeta potential of the linter cotton pulps at different of total poly(DADMAC). In this case, increasing the refining number of beating increases only very slightly of total poly(DADMAC). Thus, the total poly(DADMAC) is necessary to reach the isoelectric point of the fibres increased modestly with increasing beating level. Table 3.25 shows cationic demand of different pulps at different level of beating. In all cases, linter cotton pulps can be considered as theses containing the minimum anionic content. In fact, non refined softwood pulps required the lower concentration of poly(DADMAC) to be neutralized compared with bleached eucalyptus pulps, but they necessitate higher concentration of poly(DADMAC) to compare with softwood of Tarascon, i.e., 0.02% (w/w with respect to o.d. pulps) of poly(DADMAC). This concentration corresponds to cationic demand which corresponds to anionic content of $1.3\mu\text{mol/g}$ of cellulose (the half of that related to bleached eucalyptus pulps and the double of that established to softwood homologue).

Table 3.20 : Zeta potential of added Poly(DADMAC) for unbeaten linter cotton

Total Poly(DADMAC)		Results	
concentration (%)	V added (ml)	Zeta potential (mV)	Conductivity (mS)
0.00	0	-20.60	0.468
0.00	0.2	-15.20	0.501
0.01	0.4	-10.20	0.466
0.02	0.8	-6.90	0.462
0.02	1.0	-1.20	0.453
0.02	1.2	1.10	0.458
0.03	1.5	8.60	0.462

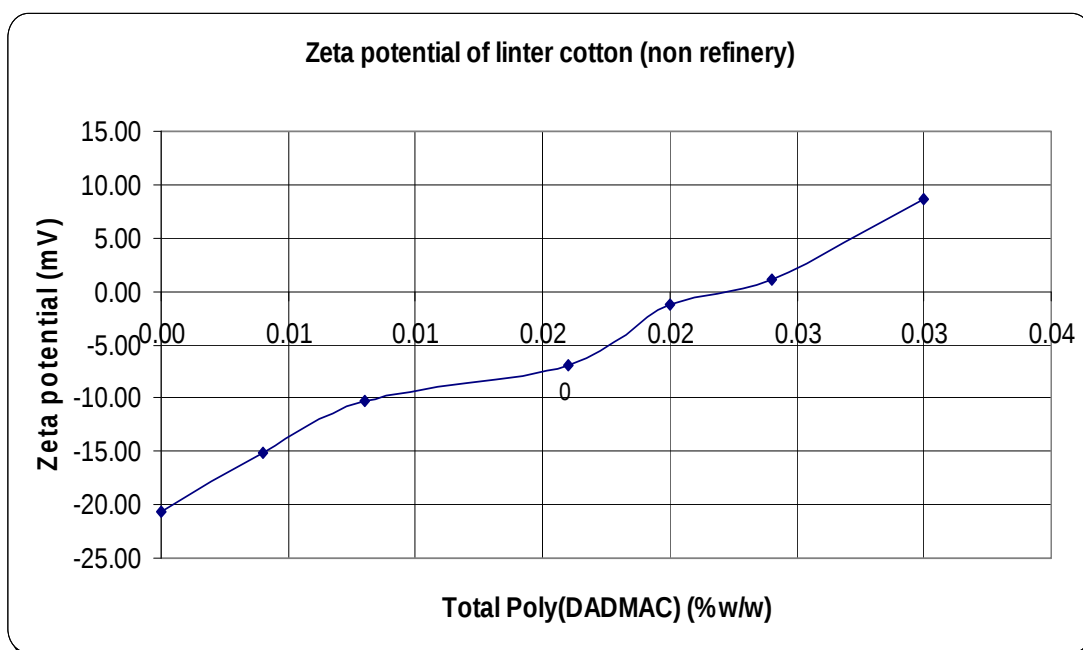
**Figure.3.32 : Zeta potential of unbeaten linter cotton**

Table 3.21 : Zeta potential of added Poly(DADMAC) for refinery linter cotton PFI 3000

Total Poly(DADMAC)		Results	
concentration (%)	V added (ml)	Zeta potential (mV)	Conductivity (mS)
0.00	0	-18.50	0.48
0.01	0.5	-11.60	0.483
0.02	0.8	-7.50	0.494
0.02	1.0	-3.60	0.485
0.02	1.2	0.00	0.496
0.03	1.5	5.80	0.498
0.00	0.0	-18.50	0.480

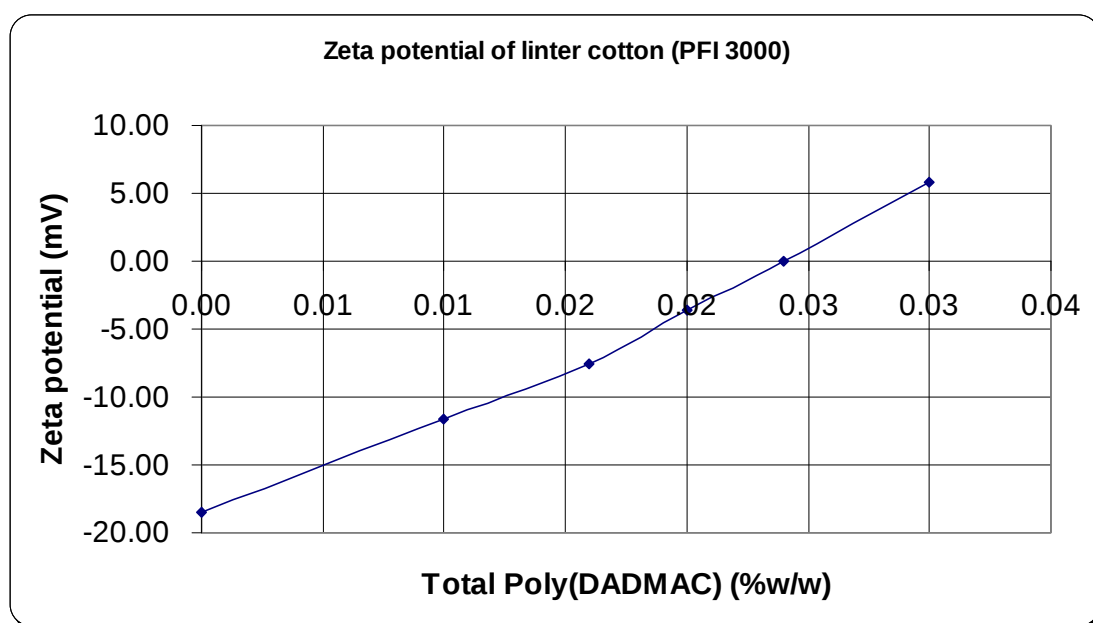


Figure 3.33 : Zeta potential of linter cotton PFI 3000

Table 3.22 : Zeta potential of added Poly(DADMAC) for refinery linter cotton PFI 6000

Total Poly(DADMAC)		Results	
concentration (%)	V added (ml)	Zeta potential (mV)	Conductivity (mS)
0.00	0	-16.80	0.532
0.01	0.5	-11.00	0.558
0.02	1.0	-3.80	0.510
0.03	1.5	1.90	0.520
0.04	2.0	7.70	0.529
0.05	2.5	12.90	0.534
0.06	3.0	18.20	0.553

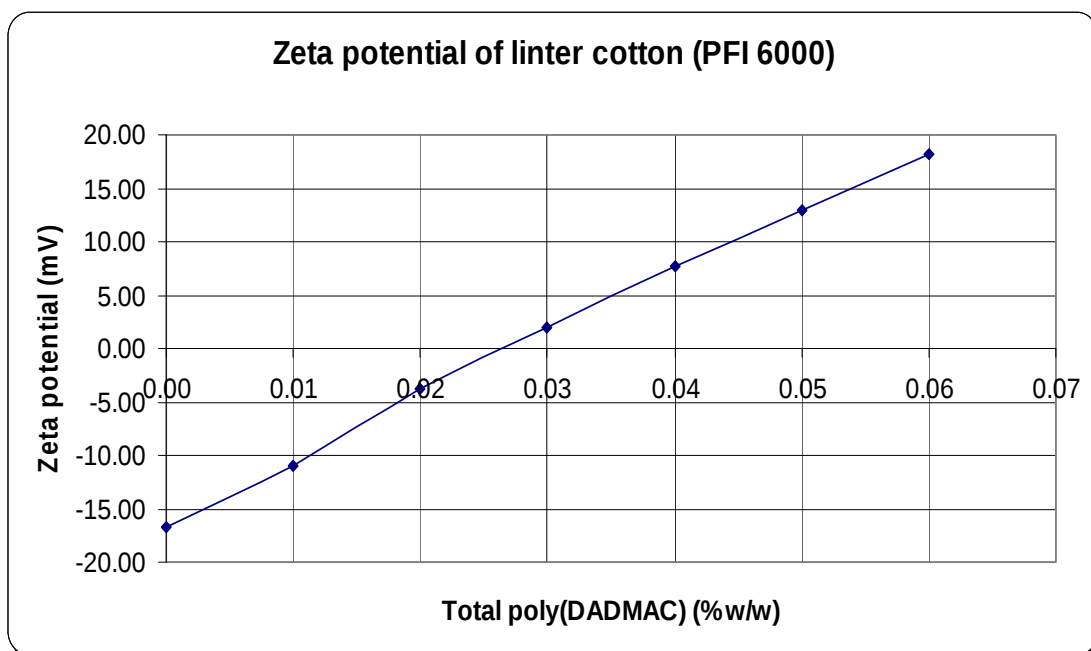


Figure 3.34 : Zeta potential of linter cotton PFI 6000

Table 3.23 : Zeta potential of added Poly(DADMAC) for refinery linter cotton PFI 10000

Total Poly(DADMAC)		Results	
concentration (%)	V added (ml)	Zeta potential (mV)	Conductivity (mS)
0.00	0	-14.80	0.519
0.01	0.5	-10.40	0.529
0.02	1.0	-5.80	0.517
0.03	1.5	1.20	0.537
0.04	2.0	4.00	0.518
0.05	2.5	9.40	0.531
0.06	3.0	15.30	0.543

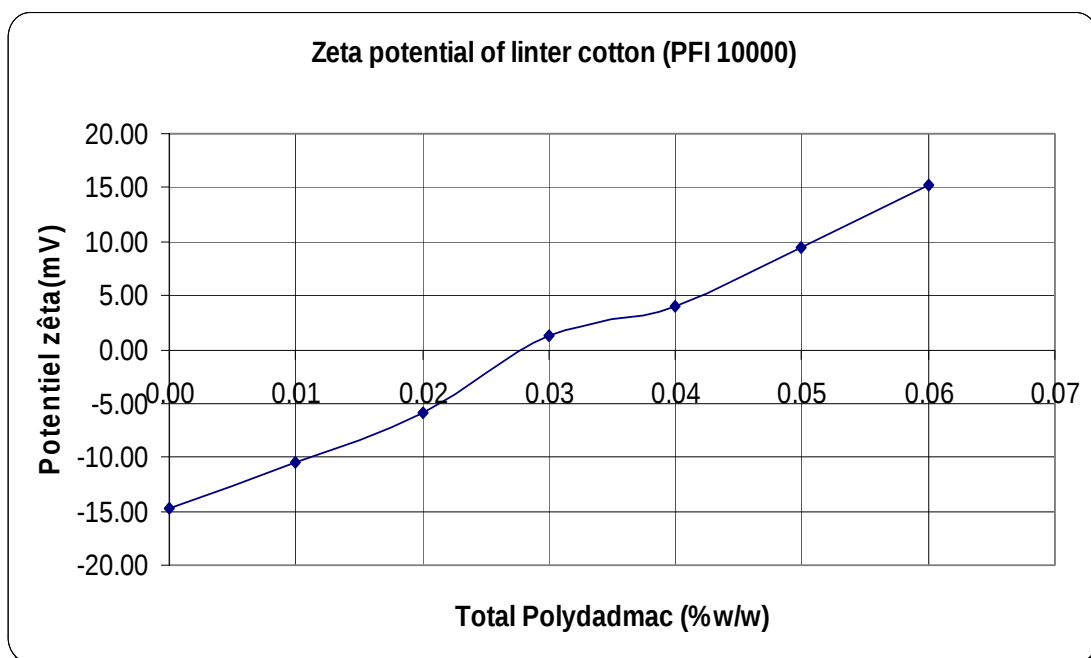


Figure 3.35 : Zeta potential of linter cotton PFI 10000

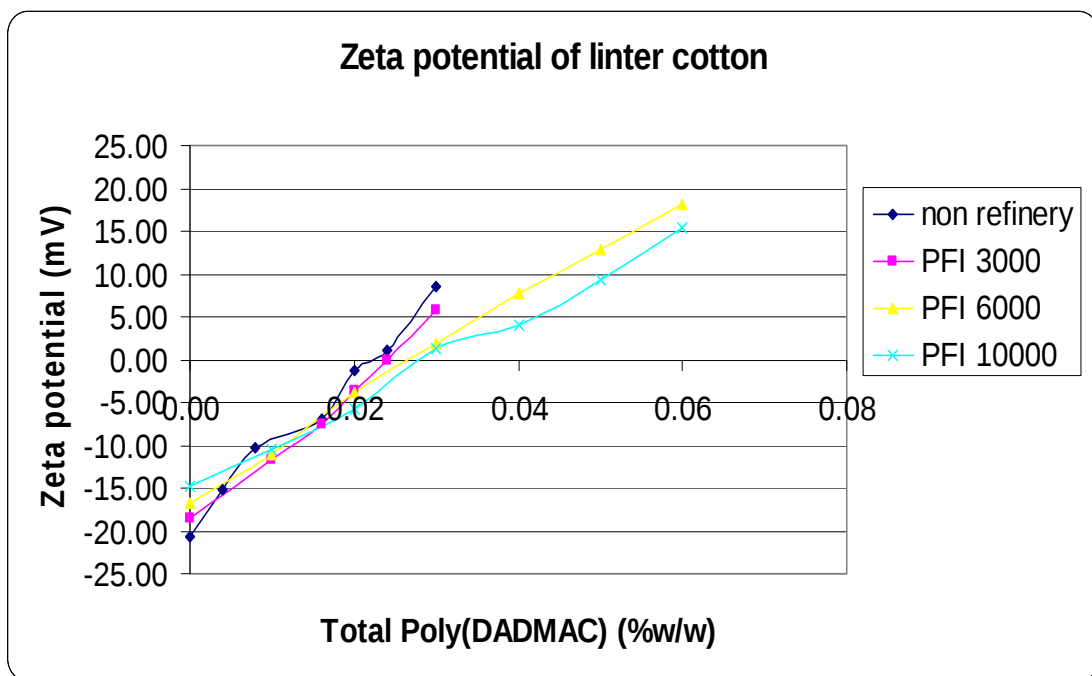


Figure 3.36 : Zeta potential of linter cotton PFI 10000

Table 3.24 : Cationic demand of linter cotton at different degrees of beating.

Linter cotton	poly(DADMAC) (% w/w)	Cationic demand ($\mu\text{eq/g}$ of cellulose)
Non refinery	0.02	1.3
PFI 3000	0.024	1.5
PFI 6000	0.027	1.7
PFI 10000	0.027	1.7

3.4. Zeta potential of pulps at different degrees of beating.

Table 3.25 summarizes the data of cationic demand and different degree of beating. The values of non refined pulps are in agreement with those reported in the literature for similar wood species [12, 14, 30-31].

Table 3.25 : Cationic demand of pulps at different degrees of beating.

Degree of beating	Cationic demand ($\mu\text{eq/g}$ of cellulose)		
	Bleaching eucalyptus	Softwood of Tarascon	Linter cotton
0	2.2	0.6	1.3
3000	7.4	3.7	1.5
6000	11.7	4.9	1.7
10000	17.0	7.4	1.7

3.5 Conclusions

We studied methylene blue adsorption on to different pulps (non refinery and refinery PFI 3000, 6000 and 10000) in suspension fiber with 0.6 mM barbitol as a medium to control pH of system. We cannot describe many much of these result as the present of adsorption isotherms as shown in normal form, this may be due to the other form such Langmuir model. Desorption of reaction may be the occurred due to the reduction of adsorption isotherm. Other possibly parameter are surface area of fiber, the size of pore, pore volume which determine by the other method such Inverse Size Exclusion Chromatography (ISEC).

We decided to do the other method such potential zeta for better understanding about this adsorption. The cationic demand corresponds to anionic groups' content in pulps that was investigated by zeta potential methods. Obviously that increasing cationic demand, the carboxyl group is higher. From these result of we cannot describe many much about these adsorption behavior, even though including of the work Missaoui [9]. This is the new first time for the adsorption behavior knowledge for these pulps.

CONCLUSION

L'objectif principal de notre travail a été l'étude des phénomènes d'adsorption en présence de bleu de méthylène comme colorant par spectroscopie de UV-Visible méthode et des propriétés électrocinétiques des fibres de cellulose par potentiel zêta méthode.

Pour ce faire, nous avons utilisé la méthode de spectroscopie (UV-Visible) et grâce à laquelle nous avons pu déterminer la variation des quantité de bleu de méthylène adsorbées en fonction de celles ajoutées. Aussi, nous avons utilisé la méthode de potentiel zêta de différent types de pâtes à différents degrés de raffinage. Trois pâtes sont choisis comme les pâte échantillons suivantes, eucalyptus blanchi, résineux de Tarascon et coton linter. Nous avons utilisé la suspension des fibres dans 0,6 mM barbital pour contrôler le pH. La réaction est très rapide pour compléter dans 2 ou 30 minutes.

Nous avons trouvé sur les résultats que l'adsorption de bleu méthylène de eucalyptus blanchi, résineux de Tarascon et coton linter (non raffinage et raffinage PFI 3000, 6000 et 10000) ne peut être pas expliqué comme l'expression normal. On a pensé que l'autre model peut être montré : Langmuir. Nous suppose qu'il y a une désorption sur isotherme d'adsorption parce que la quantité d'adsorption de bleu méthylène est descendu quand le temps de réaction est plus long. C'est difficile à expliquer plus sur l'adsorption de bleu méthylène. On pense que ça dépend de les autres paramètres par exemple la surface la nature de pâte, la taille du pore que on peut utiliser un autre méthode, ISEC, pour déterminer. En plus pour déterminer de demande cationique des pâtes par la méthode de potentiel zêta, on a trouvé que plus degré de raffinage, plus haut de cationique demande qui reflète à la quantité de groupe de anionique sauf coton linter que ce valeur est près que le même. Une raison est peut être supposée est la nature du pâte.

REFERENCES

References :

1. Nevell T.P. and Zeronian S. H., Cellulose chemistry and its applications, 1985, Ellis Horwood limited, p. 246-248.
2. TAPPI T237 os-77
3. Samuelson O. and Wennerblom A., *Svensk Papperstidning*, 1955, 19, p. 713.
4. Sobue H. and Okubo M., 1956, 39(6), p. 415.
5. Davidson, G.F. *J. Textile Inst.*, 1948, 39, T65.
6. Davidson G.F., *J. Text. Inst.*, 1950, 39, T361.
7. Slavik I., Pasleka M. and Kucerova M., *Svensk Papperstidning*, 1967, 70, 7, p. 229.
8. Slavik I., Pasleka M. and Kucerova M., *Svensk Papperstidning*, 1967, 70, 11, p. 365.
9. Missaoui M., *PhD thesis*, National Polytechnic Institute of Grenoble, France, 2005.
10. Belgacem M.N. and Gandini A., 2002a “*La chimie des substances renouvelables*”, L’Actualité Chimique Novembre-Décembre, p. 6-14.
11. Belgacem M.N. and Gandini A., “*Monomers, polymers and composites from renewable resources*”, Elsevier, Amsterdam, The Netherland, 2008.
12. Roberts.J.C., The chemistry of paper. *Departement of paper, UMIST, Manchester*, 1996.
13. Wagberg. L et Annergren. G, Physicochemical characterization of paper making fibers , dans: The fundamentals of papermaking material, transaction of the 11th fundamental research symposium at Cambridge. Septembre 1997” : *Baker, C.F., Pira international, UK*.
14. Fontaille. M et Gnanou. Y, Chimie et physicochimie des polymères: *Dunod, Paris*, 2002.
15. Scott. W.E, Abbott. J.C. and Trosset. S, “*Properties of paper: an introduction*”, *TAPPI, Atlanta, Georgia*, , 1995.

16. Donzé J. J., Colorants textiles. *Téchnique de l'ingénieur*, 1988., Ref; K-350.
17. Dogan M. and Özdemir Y., *Dyes and Pigments*, 2006, p. 1-13.
18. Kaewprasit C., Hequet E., Abidi N. and Gurlot, J.P. , *The Journal of Cotton Science* ,1998, 2, p. 164-173.
19. Fardim P. and B. Holmbom, *Tappi Journal.*, 2003, 2(10), p. 28-32.
20. Onabe F., *A systems approach to the interfacial properties in polyelectrolyte-cellulose interactions*, thesis of University of Tokyo, 1979.
21. Schaw D. J, Introduction to colloid and surface chemistry : *Butterworths-Heinemann, London-UK*, 1992.
22. Lide, D. R., "*Handbook of chemistry and Physics*", CRC Press, Boca Rota, 1995.
23. Fardim, P., Moreno, T and Holmbom, B., *Journal of Colloid and Interface Science*, 2005, 290, p. 383-391.
24. Janos P., *Environmental Science and Technology*, 2003, 37 (24), p. 5792-5798.
25. Germán-Heins, J. and Flury M., *Geoderma*, 2000, 97, p. 87-101.
26. Fengel D., Wegener G., "*Wood Chemistry Ultrastructure Reactions*", Walter de Gruyter, Berlin, 1989.
27. Rubin, E., Rodriguez P, Herrero, R., Cremades J., Barbara I. and Manuel E Sastre de Vincente., *Journal of Chemical Technology and Biotechnology*, 2005, 80, p. 291-298.
28. Otero, M., Rozada F., Calvo L.F. Garcia A. I. and Moran, A., *Biochemical Engineering Journal*, 2003, 15(1), p. 59-68.
29. Fischer K. and Heinze H., "*Hemicelluloses*", John Wiley and Sons, Weinheim, Germany, 2006.
30. Gullichsen J. and Paulapuro H., "*Papermaking Science and Technology*", Fapet Oy, Helsinki, 1999, Vol. 2 - 3.
31. Kennedy J.F., Philips G.O. and Williams P.A., "*The Chemistry and Processing of Wood and Plant Fibrous Materials*" Woodhead, Cambridge, UK, 1996.

Contribution à l'étude des phénomène d'adsorption de colorant par les fibres cellulosiques papetières : cas particulier de bleu méthylène

La présence de groupe carboxyle à la surface de fibre dans cellulose est la grande importance dans l'industrie papetière. Dans notre travail, le phénomène de l'adsorption de bleu méthylène dans la suspensions des trois pâtes par UV-Visible spectroscopie sont étudiés. Ces résultats de non raffinage et raffinage des pâtes à trois niveaux de raffinage. Nous, nous avons choisi l'eucalyptus blanchi, résineux de Tarascon et coton linter comme les pâtes échantillons. Ces résultats sont comparés. L'autre méthode telle que poentiel zêta été étudié pour mieux comprendre ce phenomène.

MOT CLES : adsorption, adsorption de bleu méthylène, polyélectrolyte, potentiel zêta

Adsorption of dyes on to cellulose

The presence of carboxyl groups at the surface of cellulose fibres is the great importance in papermaking industry. In our work the phenomenon of methylene blue adsorption in the pulps suspensions of three different pulps by UV-Visble spectroscopy are studied. These results of non refinery and refinery pulps of bleached eucalyptus, softwood of Tarascon and linter cotton were compared. Other method such as zeta potential was investigated to better understanding of this phenomenon.

KEY WORDS : adsorption, methylene blue adsorption, polyelectrolyte, zeta potential