Carbohydrate Polymers 84 (2011) 299–307

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Alkali treatment of cellulose II fibres and effect on dye sorption

Ján Široký[a,b], Richard S. Blackburn[a,*], Thomas Bechtold[b], Jim Taylor[c], Patrick White[c]

[a] *Green Chemistry Group, Centre for Technical Textiles, University of Leeds, Leeds, LS2 9JT, UK*
[b] *Christian Doppler Laboratory for Textile and Fibre Chemistry in Cellulosics, Research Institute of Textile Chemistry and Textile Physics, University of Innsbruck, Höchsterstraße 73, A-6850, Dornbirn, Austria*
[c] *Lenzing Fibers, Lenzing Aktiengesellschaft, 4860 Lenzing, Austria*

ARTICLE INFO

Article history:
Received 15 July 2010
Received in revised form
16 November 2010
Accepted 17 November 2010
Available online 24 November 2010

Keywords:
Freundlich isotherm
Langmuir isotherm
Adsorption
Polysaccharides
Lyocell
Sodium hydroxide
Hydrolyzed reactive dye
Reactive structural fraction (RSF)

ABSTRACT

To understand the effect of alkali treatment on sorption behaviour of cellulose II fibres, samples were continuously pre-treated using NaOH over a concentration range of 0.0–7.15 mol dm^{-3}, with varying tension; treated substrates were dyed with hydrolysed C. I. Reactive Red 120. Greatest adsorption of dye occurs for cellulose II fibres treated with 2.53 and 3.33 mol dm^{-3} aqueous NaOH solution. Correlation to sorption isotherms is most closely associated with a Langmuir type isotherm, but correlation to the Freundlich isotherm is still significant, indicating sorption *via* a combination of Langmuir and Freundlich isotherms. Adsorption energy (ΔG^0) increases with increasing NaOH concentration to a maxima between 2.53 and 3.33 mol dm^{-3} NaOH and then decreases with further increase in NaOH concentration. Equilibrium dye sorption shows good correlation with water sorption as assessed by the reactive structural fraction (RSF) theory. Theoretical monolayer capacity (q_0) increases with increasing NaOH concentration to a maxima at 3.33 mol dm^{-3} NaOH and then decreases with further increase in NaOH concentration; q_0 is significantly in excess of the number of available specific sites ($-COO^-Na^+$) in the substrate, indicating non-site-specific interactions, more typical of a Freundlich isotherm. Pores in the fibre significantly affected by alkali treatment (<20 Å diameter) and accessibility of dye (14 Å) sorption into those pores account the differences observed herein; maximum q_e, q_0 and ΔG^0 are observed for cellulose II fibre treated with 2.53–3.33 mol dm^{-3} NaOH as this concentration range affects the greatest increase in accessible pore volume in the fibres.

1. Introduction

Cellulose is the most abundant biopolymer (Klemm, Heublein, Fink, & Bohn, 2005) and of particular interest in providing renewable, sustainable, biodegradable biopolymers for industrial applications. Cellulose is a linear 1,4-β-glucan polymer where the units are able to form highly ordered structures, this occurs as a result of extensive interaction through intra- and intermolecular hydrogen bonding of the three hydroxyl groups in each cellulose unit. Treatment of cellulose with aqueous sodium hydroxide (NaOH) solutions has a substantial influence on morphological, molecular and supramolecular properties of cellulose, causing changes in crystallinity, pore structure, accessibility, stiffness, unit cell structure and orientation of fibrils in cellulosic fibres (Goswami, Blackburn, El-Dessouky, Taylor, & White, 2009). Treatment with alkali can improve mechanical and chemical properties of cellulose fibres, such as dimensional stability, fibrillation tendency, tensile strength, dyeability, reactivity, lustre and fabric smoothness.

Lyocell fibres are produced by regenerating cellulose I (typically sourced from eucalyptus trees) into fibre from a solution in an organic solvent (Albrecht, Reintjes, & Wulfhorst, 1997). Solvent-spun lyocell fibres consist of crystalline cellulose II and amorphous cellulose, and have a higher degree of crystallinity (80%) in comparison with other regenerated cellulosic fibres, such as modal (49%) and viscose (41%) (Heinze & Wagenknecht, 1998). The high degree of crystallinity in lyocell is a consequence of higher orientation during stretching and formation of fibres; lyocell fibres have the thinnest and longest crystallites of all cellulosic fibres, even the amorphous regions are oriented along the fibre axis (Kreze & Malej, 2003). Lyocell fibres spun from cellulose solution in *N*-methylmorpholine-*N*-oxide (NMMO) hydrate have proven commercially successful in textile products due to their excellent mechanical properties in the wet state; the fibres also have excellent environmental credentials (Goswami et al., 2009; White, Hayhurst, Taylor, & Slater, 2005). Lyocell fibres have a microfibrillar structure because a portion of the molecular chains aggregate to form microcrystals while recrystallizing along the chains, whereas the remaining chains exist in the amorphous phase as links between these two phases (Okano & Sarko, 1984). In the crystalline regions of cellulose II polymers, the layered structure is very regular

---

[*] Corresponding author. Tel.: +44 0 113 343 3757; fax: +44 0 113 343 3704.
E-mail address: r.s.blackburn@leeds.ac.uk (R.S. Blackburn).

0144-8617/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2010.11.037

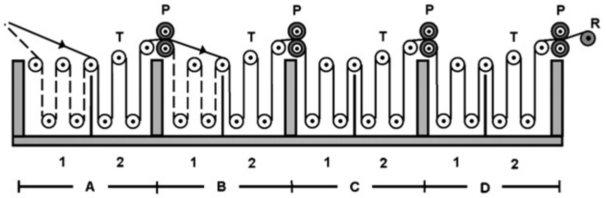


Fig. 1. Schematic illustration of apparatus used in continuous alkali pre-treatment process.

with an antiparallel arrangement of cellulose chains with some inter-sheet hydrogen bonding, generally leading to a perfectly distributed symmetrical structure; however, the hydrogen-bonded network is complicated and debate is ongoing as to the absolute structure (Gessler et al., 1995; Kolpak & Blackwell, 1976; Kono & Numata, 2004; Langan, Nishiyama, & Chanzy, 1999; Raymond, Heyraud, Tran Qui, Kvick, & Chanzy, 1995). During the formation of lyocell fibres, a so-called 'quasi-crystalline' phase readily forms, where polymer orientation is relatively low to moderate, compared with the crystalline phase; this quasi-crystalline phase is attributed to the presence of imperfect microcrystals and co-exists with the amorphous phases (Langan et al., 1999). Based on this three-phase structure of lyocell fibres, it has been proposed (Zhu, Ren, & Wu, 2004) that alkali can only permeate into the quasi-crystalline and amorphous phases, leading to disassociation of the quasi-crystallites. However, based on the work of Okano and Sarko (1984, 1985), at higher concentrations the fully crystalline phases must convert to phases of lower crystallinity; it is unclear as to whether crystalline regions have a transitional phase through a quasi-crystalline phase, but this is certainly worthy of investigation. Hence, changes in lyocell crystallinity depend upon transformation of the crystalline and quasi-crystalline phases, and whether these phases transform into less oriented states as crystallinity decreases. Recently, Goswami et al. (2009) observed that sodium hydroxide treatment causes the density, orientation and crystallinity of lyocell fibre to decrease with increasing sodium hydroxide concentration, and that the greatest change in fibre properties occurs between 3.0 and 5.0 mol dm^{-3} NaOH. This was attributed to the onset of formation of sodium (Na)-cellulose II at 3.0 mol dm^{-3} NaOH; a fully formed Na-cellulose II structure was observed above 6.8 mol dm^{-3} NaOH. The work concludes that formation of Na-cellulose II causes plasticization of the lyocell fibres as both inter and intra-molecular hydrogen bonds are broken by these high sodium hydroxide concentrations.

Regenerated cellulosic fibres absorb significant quantities of water by the expansion of void spaces within the semi-crystalline morphology, forming a water-cellulose two-phase structure. Dyestuffs for cellulosic fibres are highly water soluble, with molecular structures designed to interact at the internal interface between cellulose and water. The uptake of dyes is often used to monitor changes in fibre properties brought about by variations in processing, hence, dyes can be considered as coloured probe molecules that provide information on the detailed internal pore structure of fibres (Ibbett, Kaenthong, Phillips, & Wilding, 2006). Despite several classes of dyes being suitable for application to cellulosic fibres, around 50% of all cellulosic fibres globally are dyed with reactive dyes (Roessler & Jin, 2003).

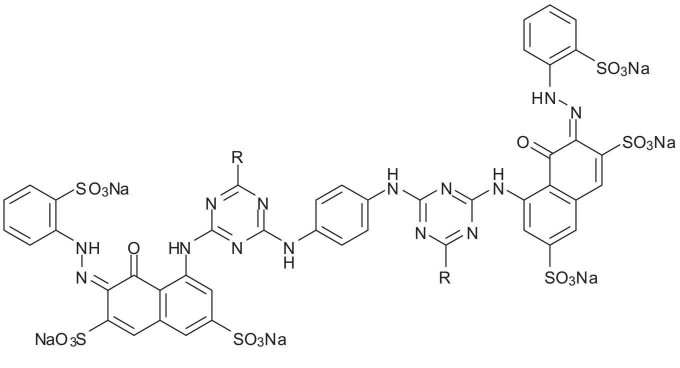
Researchers have concluded that when cellulose I is converted to cellulose II the crystallinity index decreases, therefore, it is interesting to understand the change in crystallinity of cellulose II polymers when treated in alkali, particularly considering the increasing importance of lyocell fibres in the textile industry. There is significantly limited research concerning the effect that alkali treatment of cellulose II polymers has on fibre sorption, particularly adsorption of dye molecules from an aqueous environment.

This paper examines the adsorption of reactive dyes on lyocell fibres to understand the effect that alkali treatment has on the thermodynamics of the sorption system; the use of dyes as probes can also provide information on changes in the fibre structure.

2. Experimental

2.1. Materials

Plain woven, desized, scoured lyocell fabrics, 1/1 weave, 140 g m^{-2} with 35 ends and 28 picks cm^{-1}, comprised of 30/1 Nm yarn, was used in this research and was supplied by Lenzing AG, Austria. *Lyogen MC* was supplied by Clariant, Switzerland. C. I. Reactive Red 120 (RR120; **1**) was kindly supplied by DyStar, Germany. All other chemicals were laboratory grade supplied by Aldrich.



1 R = Cl
2 R = OH

2.2. Continuous alkali pre-treatment

Fabric samples (5.0 × 0.2 m) were conditioned at 65 ± 4% relative humidity (RH) and 20 ± 2 °C for at least 48 h prior to treatment. The continuous process of alkali pre-treatment was conducted using apparatus as depicted schematically in Fig. 1. The apparatus was divided into four compartments (A, B, C, and D), each with two sub-compartments (1 and 2) that could be heated independently; the four stages were alkali treatment (A), stabilization treatment (B), washing (C), and neutralization (D). The fabric was passed through the apparatus over a series of rollers including tension compensators (T) and pressurized squeeze rollers (P). The solid line represents the usual route of fabric passage through the machine, while the dashed line represents the route employed in some instances. The fabric after passing through the last compartment (D) was wound on a take-up roller (R).

Sodium hydroxide concentration in the alkali treatment bath was varied, using concentrations of 0.0, 2.25, 3.0, 3.75, 5.0, and 7.0 mol dm^{-3}; in the alkali treatment bath 1 g dm^{-3} *Lyogen MC* was added, which is an alkali-stable surfactant and wetting agent. Sodium hydroxide in the stabilization stage was 20% of the concentration in the alkali treatment bath, i.e. 0, 0.45, 0.6, 0.75, 1.0, and 1.4 mol dm^{-3}, respectively. Due to changes in the concentration in the first treatment stage, the "effective" concentration of alkali was established at 0.0, 2.53, 3.33, 4.48, 4.65 and 7.15 mol dm^{-3} for treatment bath and 0.0, 0.73, 1.08, 1.18, 1.48 and 2.15 mol dm^{-3} for stabilization bath, which is described in detail in our previous work (Široký et al., 2009). Washing was performed in water alone at 80 °C; neutralization was carried out using 2 g dm^{-3} acetic acid (80%, v/v) at 80 °C. After the treatment process, samples were dried continuously in a stenter at 130 °C, but not as part of the continuous treatment.

Tension in compartment A was applied at either 49 N m^{-1} or 147 N m^{-1}, tension in compartment B was applied at 147 N m^{-1}, and tension in compartments C and D was applied at 49 N m^{-1}. During the alkali treatment stage the temperature of the solution was set at 40 °C, and in the stabilization stage the temperature was 60 °C. In each compartment, the volume of the liquor was 20 dm^3. The speed of passage of fabric through the system was set at 2 m min^{-1}. Further details about the conditions and adjustments of continuous alkali pre-treatments are available in our previous work (Široký et al., 2009).

2.3. Dyeing

Prior to dyeing, a 1% aqueous solution of RR120 was hydrolyzed at pH 11.5 (NaOH) at 80 °C for 120 min to ensure full hydrolysis, and then cooled and the solution neutralized (HCl), forming compound **2**. Hydrolyzed RR120 (**2**; 1431.9 g mol^{-1}) was used for sorption experiments rather than the parent dye to ensure that covalent reaction between the dye and fibre did not interfere with sorption; the hydrolyzed reactive dye behaves essentially like a direct dye. This provides particular advantages: the substantivity (physical adsorption) for the cellulose substrate is high, so relatively short dyeing times can be employed; these dyes can be used as molecular sensors to characterize cellulose substrate properties, *e.g.* pore structure (Inglesby & Zeronian, 2002; Luo, Zhang, & Chen, 2003).

Subsequently, alkali pre-treated lyocell fabrics (2.5 g) were dyed with the hydrolyzed reactive dye at pH 7 at varying concentrations (0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0% omf) in a *Roaches Pyrotec S Rotodyer* dyeing machine, using a liquor-fibre ratio of 20:1. Alkali pre-treated lyocell fabrics were introduced to the dyebath at the dyeing temperature (70 °C), which contained 40 g dm^{-3} NaCl, and held for 120 min. Previously, these dyeing conditions have been employed on such substrates with this hydrolyzed dye for a total dyeing time of 24 h; aliquots of the dyeing liquor were analysed periodically using UV/visible spectrophotometry, and it was determined that equilibrium in this system is achieved after 90 min. Hence for expediency, all dyeings herein were held for 120 min, this time being sufficient to achieve sorption equilibrium based on this previous experience, and is in agreement with other researchers (Ibbett, Kaenthong, et al., 2006; Ibbett, Phillips, & Kaenthong, 2006; Wang & Hauser, 2009; Zhou, Yeung, Yuen, & Zhou, 2003), for sorption studies on cellulosic substrates under very similar conditions; Carrillo, Lis, & Valldeperas (2002) demonstrated that the time to achieve equilibrium for C. I. Direct Blue 1 on lyocell fibres was 55 min at 120 °C.

2.4. UV/visible spectrophotometry

From the exhausted application baths, the equilibrium dye concentration in solution (C_e; mg dm^{-3}), was calculated directly from absorption of the dye solution after dyeing, according to The Beer–Lambert Law. Absorption of residual dyebaths at the end of dyeing was measured using a *Jasco V-530* UV/visible/NIR spectrophotometer at 512 nm, the wavelength of maximum absorption (λ_{max}) for the dye, at 2 nm intervals. Concentrations were calculated from calibration graphs. Equilibrium concentration of dye on the sorbent (cellulose II) (q_e; mg g^{-1}) was calculated by subtracting C_e from the initial concentration of dye at the start of the dyeing process (C_0) and accounting for the liquor:fibre ratio. Blank dyebaths without fibre were taken through the dyeing process and it was demonstrated that the concentration of the dye did not change over the process in the absence of substrate.

2.5. Computational chemistry

The geometry and the electronic properties of hydrolyzed RR120 (**2**) were explored using quantum mechanics methods (DFT/BPW91/6-31+G(d)) employing Gaussian 03 software (Fig. 2a); the electrostatic potential of hydrolyzed RR120 was plotted on top of a total electron density isosurface (Fig. 2b).

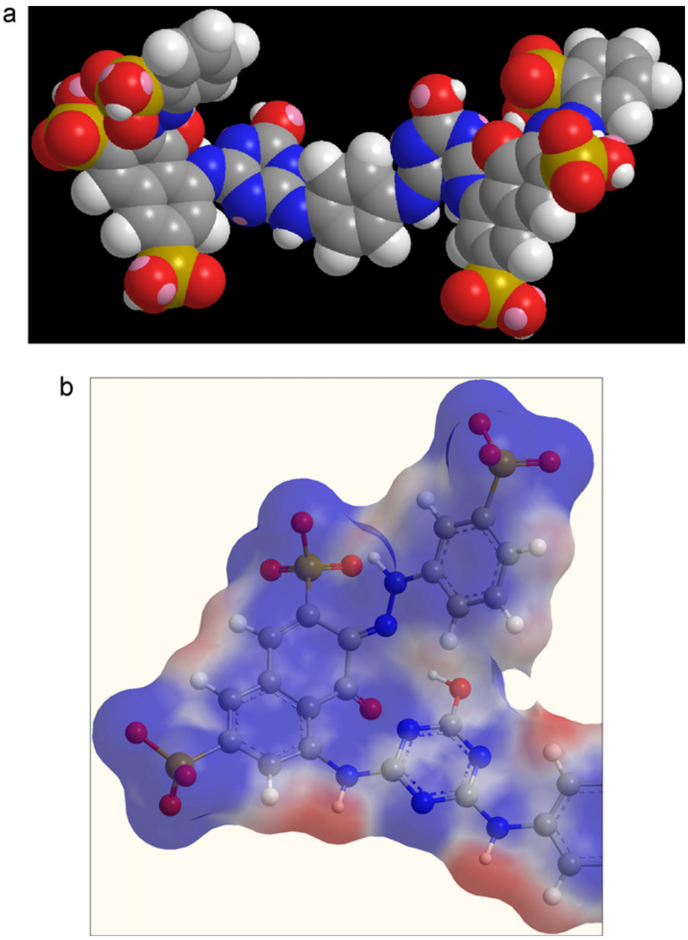


Fig. 2. (a) Molecular structure of hydrolysed RR120 (**2**) as calculated by molecular dynamics; (b) electrostatic potential plotted onto a total electron density isosurface for hydrolyzed RR120 (half molecule shown, dissected down centre). Blue is used to represent the strongest negative electrostatic potential on the molecule and red the strongest positive electrostatic potential. The other colours are the values in between, white is neutral. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

In previous research, Blackburn, Harvey, Kettle, Payne, and Russell (2006) modelled a partially oxidized cellulose I (cotton) surface by cleaving a layer of glucose chains from the crystal structure, adding an anionic carboxylate group (COO$^-$), and introducing a Na$^+$ counterion; it was demonstrated that the Na$^+$ counterion is preferentially located to have interactions with the COO$^-$ group. Herein similar principles are applied to estimate geometry and electronic properties in a lyocell (cellulose II) surface by calculating the Connolly surface (Connolly, 1983) (at the van der Waals radii) for a periodic cellulose II system. The geometry and the electronic properties of a glucose unit and a glucose unit where the C6 position is oxidized to a COO$^-$ group and a Na$^+$ counterion introduced were explored and the electrostatic potential of these two moieties was plotted on top of a total electron density isosurface (Fig. 3).

3. Theoretical basis

3.1. Equilibrium model

In order to fully understand the sorption system involved between the dye and cellulose II, it is important to establish the most appropriate correlation for the equilibrium curves, which can

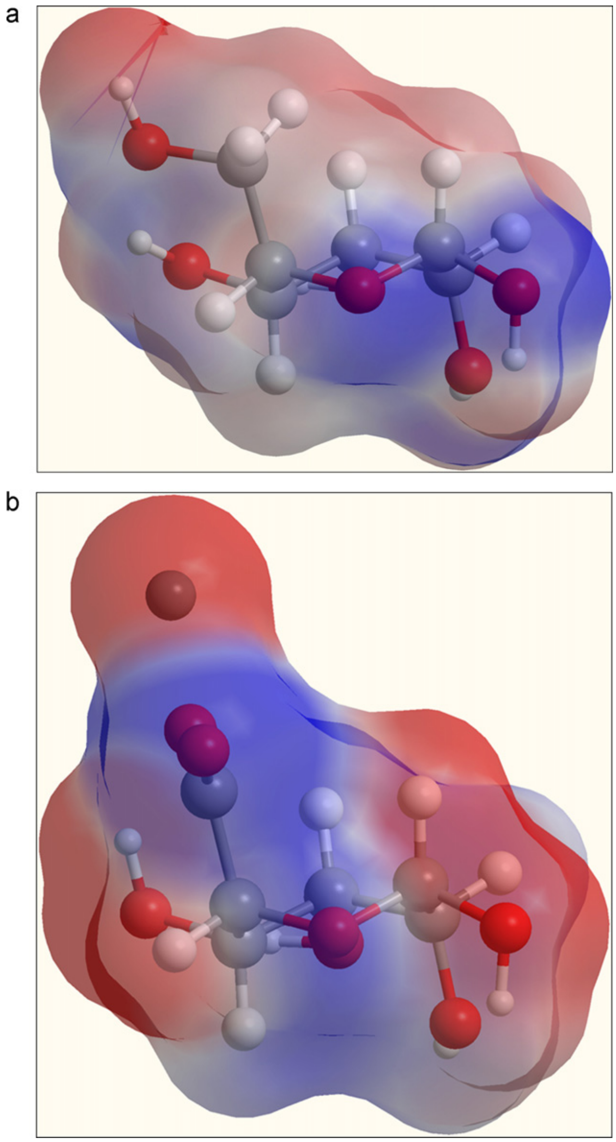


Fig. 3. Electrostatic potential plotted onto a total electron density isosurface for (a) glucose and (b) glucose with COO⁻ group at C6 position with Na⁺ counter-ion. Blue is used to represent the strongest negative electrostatic potential on the molecule and red the strongest positive electrostatic potential. The other colours are the values in between, white is neutral. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

be obtained by measuring the sorption isotherm of the dye onto cellulose II using experimental data.

3.2. *Langmuir isotherm*

The Langmuir isotherm describes sorption onto specific homogeneous sites within an adsorbent (Langmuir, 1916, 1918). Langmuir's model of adsorption depends on the assumption that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate (the dye) at the outer surface of the adsorbent (cellulose II). It is then assumed that once a sorbate molecule occupies a site, no further adsorption can take place at that site. Moreover, the Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent and there is no interaction between molecules adsorbed on neighbouring sites. Theoretically, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further sorption can take place. The saturated or monolayer (as $C_t \to \infty$) capacity can be represented by the expression represented in Eq. (1):

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{1}$$

where q_e is the equilibrium concentration of sorbate on the sorbent (solid-phase) ($\mathrm{mg\,g^{-1}}$), C_e is the equilibrium sorbate concentration in solution ($\mathrm{mg\,dm^{-3}}$), K_L ($\mathrm{dm^3\,g^{-1}}$) and a_L ($\mathrm{dm^3\,mg^{-1}}$) are Langmuir constants. The constants K_L and a_L are evaluated through linearization of Eq. (1) (Eq. (2)).

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{2}$$

Therefore, a plot of C_e/q_e versus C_e should yield a straight line of intercept value $1/K_L$ and slope a_L/K_L if the isotherm obtained through experimental observes the Langmuir expression. The theoretical monolayer capacity is q_0 ($\mathrm{mg\,g^{-1}}$) and is numerically equal to K_L/a_L. However, the linearity of Eq. (1) is only respected at low solution concentrations, where the model follows Henry's law: as C_e becomes lower, $a_L C_e$ is much less than unity and $q_e = K_L C_e$.

3.3. *Freundlich isotherm*

The Freundlich isotherm (Freundlich, 1906) suggests that sorption energy exponentially decreases on completion of the sorptional centres of an adsorbent and describes heterogeneous systems, which are characterized by the heterogeneity factor $1/n_F$. When $n = 1/n$, the Freundlich equation reduces to Henry's law. Hence, the empirical equation (Eq. (3)) can be written:

$$q_e = K_F C_e^{1/n_F} \tag{3}$$

where q_e is the equilibrium concentration of sorbate on the sorbent (solid-phase) ($\mathrm{mg\,g^{-1}}$), C_e is the equilibrium sorbate concentration in solution ($\mathrm{mg\,dm^{-3}}$), K_F is the Freundlich constant ($\mathrm{dm^3\,g^{-1}}$), and $1/n_F$ is the heterogeneity factor. The capacity constant K_F and the affinity constant n_F are empirical constants dependant on several environmental factors. A linear form of the Freundlich isotherm can be obtained by taking logarithms of Eq. (3) (Eq. (4)).

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \tag{4}$$

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ should yield a straight line of intercept value $\ln K_F$ and slope $1/n_F$ if the isotherm obtained experimentally observes the Freundlich expression; if $n > 1$, then the adsorption is favourable. The Freundlich isotherm is another form of the Langmuir approach for adsorption on an "amorphous" surface where the amount of adsorbed material is the summation of adsorption on all sites. The Freundlich isotherm is derived by assuming an exponential decay energy distribution function inserted into the Langmuir equation. It describes reversible adsorption and is not restricted to the formation of the monolayer.

Thermodynamic data such as adsorption energy can be obtained from the Langmuir and Freundlich equations using Eq. (5), where K is constant in terms of $\mathrm{dm^3\,mol^{-1}}$ (Kim, Kim, Choi, Rengraj, & Yi, 2004).

$$-\Delta G^0 = RT \ln K \tag{5}$$

4. Results and discussion

Results from UV/visible spectrophotometric analysis of residual dye solution in the exhausted application bath (Fig. 4) demonstrated that as the concentration of dye applied increases the concentration of dye adsorbed also increases. It is observed that greatest adsorption of dye onto the substrate at equilibrium (q_e) occurs for cellulose II fibres treated with 3.33 and 2.53 $\mathrm{mol\,dm^{-3}}$

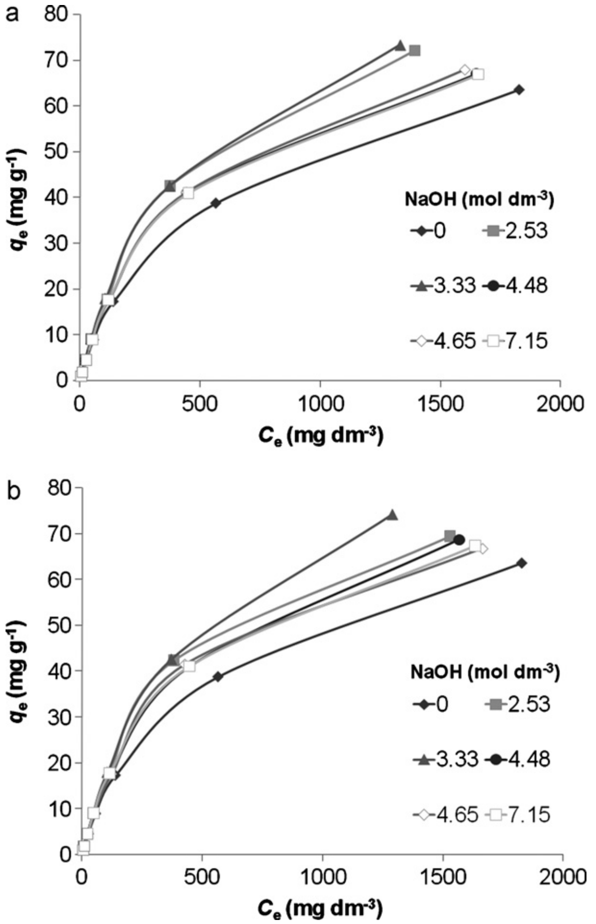


Fig. 4. Adsorption isotherm of hydrolysed RR120 sorbed onto cellulose II treated with varying concentrations of NaOH, under applied tension of (a) 49 N m^{-1} and (b) 147 N m^{-1}.

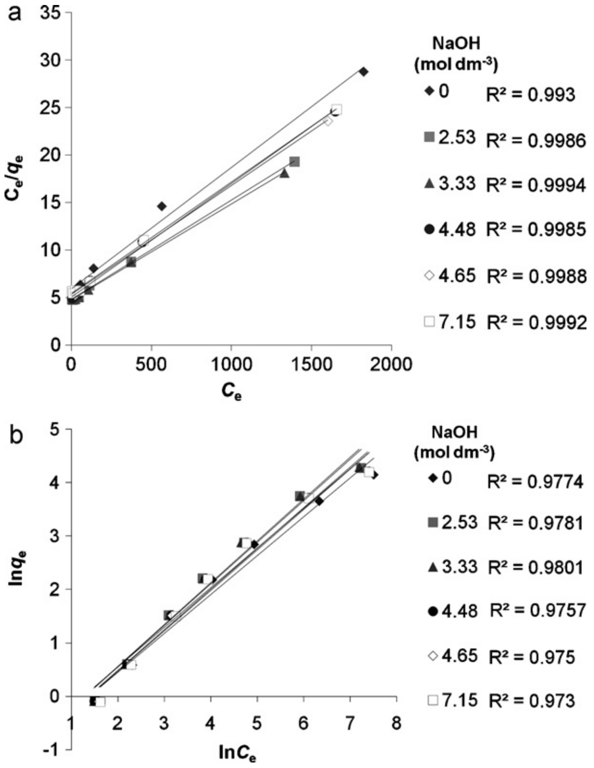


Fig. 5. Linearized isotherms of hydrolysed RR120 sorbed onto cellulose II treated with varying concentrations of NaOH, according to (a) Langmuir and (b) Freundlich isotherms (only samples treated at 49 N m^{-1} shown).

aqueous NaOH solution; there was little observed difference between applied tension in the treatment stage.

Thermodynamics of dyeing is a complex issue and many parameters have to be considered. Shore (1995) described the importance of the relative proportion, size and the shape of crystalline and amorphous regions in cellulose I (cotton) fibres, but the added factor of quasi-crystalline regions in cellulose II polymers only adds complication; additionally, changes in pore structure (shape and size) caused by alkali treatment require consideration (Bredereck & Hermanutz, 2005). Diffusion and adsorption of dyes are presumed to depend upon the extent of the accessible disordered regions in fibres, in some instances absorption may occur on the accessible surfaces of the crystallites, however, physical chemistry of dyeing theory suggests that dye molecules are not generally absorbed within fibre crystallites (Holme, 1976; Peters & Ingamells, 1973). However, examination of the fine structure of cellulose polymers reveals a range of degrees of order in the packing of chain molecules, where there is a continuous transition from perfectly crystalline to completely amorphous material through paracrystalline and quasi-crystalline regions (Nevell, 1995), this theory being particularly applied to cellulose II polymers (Langan et al., 1999). In paracrystalline regions, the three-dimensional lattice is defined by short and medium range ordering with a lack of long range order giving several sub-regions from quasi-crystalline to a more diffuse type with partially crystalline features to totally diffuse amorphous structure (Hosemann, 1950; Hosemann, Willmann, & Roessler, 1972; Voyles et al., 2001). Another interesting concept is that of *reacting structural fraction* (RSF), developed and established by Fink, Dautzenberg, Kunze, and Philipp (1986), which can provide a more detailed understanding of NaOH and water sorption at low alkali concentrations onto cellulose, changes in crystalline and non-crystalline regions that occur due to alkali treatment, and the application of NaOH to activate disordered regions of cellulose (Fink et al., 1986; Heinze & Pfeiffer, 1999). The RSF is composed of: AGUs located in the amorphous regions of the cellulose polymer; crystalline regions cellulose converted to Na-cellulose I at the NaOH concentration in question; surfaces of the remaining cellulose I crystallites (Fink et al., 1986).

The sorption isotherms were linearized by application of the theory from Langmuir and Freundlich isotherms (Fig. 5) and sorption constants and correlation coefficient (R^2) for Freundlich and Langmuir isotherms applied to this experimental data are shown in Table 1. Summarily, it is observed that correlation of the experimental data is most closely associated with a Langmuir type isotherm ($R^2 \geq 0.9930$), indicating limited, site-specific adsorption (initial exponential rise and then very slow increase). However, although the correlation coefficient for the Freundlich isotherm achieved lower values, correlation is still significant (R^2 0.9875–0.9730), which is typical of unlimited adsorption at non-specific sites.

It is interesting to relate the observations for sorption of dye from aqueous solution onto a cellulose II substrate that has been treated with increasing concentrations of NaOH to the RSF concept. Using cotton linters, Fink et al. (1986) demonstrated that at low concentrations of NaOH, the specific water sorption (H_2O-sorption per AGU for the RSF) exceeds integral values (H_2O-sorption per AGU for the whole sample), with a maximum at the commencement of lattice transition from cellulose I; this then decreases within the transition range merging in the integral sorption curve at 3.25–3.50 mol dm^{-3} NaOH; and finally rises to a second maximum at 3.50–3.75 mol dm^{-3} NaOH, well known from the integral water sorption curve. Fink et al. related this second maximum to

Table 1
Summary of the isotherm constants and correlations for Freundlich and Langmuir isotherms applied experimental data.

Tension in compartment A ($N\,m^{-1}$)	NaOH concentration ($mol\,dm^{-3}$)	Freundlich				Langmuir			
		K_F ($dm^3\,mol^{-1}$)	n_F	R^2	ΔG^0 ($kJ\,mol^{-1}$)	K_L ($dm^3\,mol^{-1}$)	$q_0 \times 10^{-5}$ ($mol\,g^{-1}$)	R^2	ΔG^0 ($kJ\,mol^{-1}$)
49	0.00	526	1.37	0.9774	−17.9	243	5.46	0.9930	−15.7
49	2.53	524	1.29	0.9781	−17.9	297	6.72	0.9986	−16.2
49	3.33	522	1.28	0.9801	−17.8	301	6.91	0.9994	−16.3
49	4.48	564	1.35	0.9757	−18.1	285	5.82	0.9985	−16.1
49	4.65	510	1.32	0.9750	−17.8	270	6.07	0.9988	−16.0
49	7.15	503	1.32	0.9730	−17.7	265	5.97	0.9992	−15.9
147	0.00	526	1.37	0.9774	−17.9	243	5.46	0.9970	−15.7
147	2.53	557	1.32	0.9757	−18.0	300	6.18	0.9994	−16.3
147	3.33	514	1.27	0.9875	−17.8	299	7.13	0.9991	−16.3
147	4.48	538	1.33	0.9775	−17.9	280	6.13	0.9975	−16.1
147	4.65	546	1.34	0.9749	−18.0	281	5.87	0.9998	−16.1
147	7.15	553	1.34	0.9826	−18.0	284	5.87	0.9992	−16.1

alkali cellulose modification from Na-cellulose I to Na-cellulose II associated with an increase of the disordered fraction.

When data from Fink et al. (1986), is compared with equilibrium dye sorption (q_e) of hydrolyzed RR120 by cellulose II fibres treated with varying concentrations of NaOH, it is observed that the trends are very similar (Fig. 6a). It is noted that the variations occur at different concentrations of NaOH, but the shape of the plots are comparable; concentration differences can be explained relative to the adsorbing substrate – Fink et al. used cellulose I fibre, herein cellulose II fibre is used. The first maximum occurs at *ca.* 2.75 mol dm^{-3} NaOH for cellulose I, and at *ca.* 3.50 mol dm^{-3} NaOH for cellulose II; this represents the first transition phase for each fibre to their respective Na-cellulose form. Subsequent decrease within the respective transition ranges then occurs to *ca.* 3.25 mol dm^{-3} NaOH for cellulose I, and to *ca.* 4.50 mol dm^{-3} NaOH for cellulose II. A second maximum occurs at *ca.* 3.75 mol dm^{-3} NaOH for cellulose I, and at *ca.* 4.75 mol dm^{-3} NaOH for cellulose II. As described above, for cellulose I this is associated with transition from Na-cellulose I to Na-cellulose II, however, for cellulose II, the fibre at such NaOH concentrations is already in the Na-cellulose II form, so no transition to a different cellulose form can occur. Goswami et al. (2009) demonstrated that, when treated with aqueous NaOH solution, the main changes in cellulose II crystallinity occur between 3.0 and 5.0 mol dm^{-3}; it is proposed that the first maximum observed herein relates to the transition from cellulose II to Na-cellulose II wherein intermolecular hydrogen bonds are broken, and the second maximum is caused by an additional increase in the RSF of the polymer, relative to disruption of the intramolecular hydrogen bonds in the Na-cellulose II form. This is evidenced from our previous work (Široký, Blackburn, Bechtold, Taylor, & White, 2010), where we have demonstrated using ATR-FTIR of cellulose II fibres treated with aqueous sodium hydroxide solution that minimum values in hydrogen-bond intensity (HBI; closely related to the well ordered crystalline phase) also occur in the region 4.50–4.75 mol dm^{-3} NaOH.

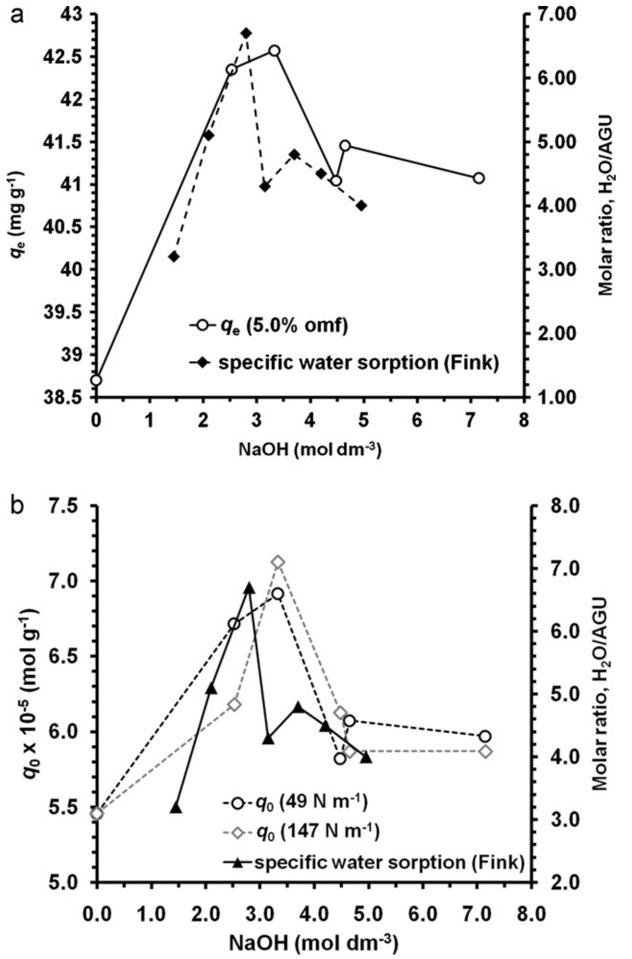


Fig. 6. (a) Equilibrium sorption (q_e) of hydrolyzed RR120 (5% omf shown) by cellulose II fibres treated with varying concentrations of NaOH; (b) theoretical monolayer capacity (q_0) of cellulose II fibres treated with varying concentrations of NaOH, under applied tension of 49 N m^{-1} and 147 N m^{-1}. Both (a) and (b) are compared with specific water sorption (molar ratio, H$_2$O/AGU) for cellulose I fibres treated with varying concentrations of NaOH, after Fink et al. (1986).

For the Langmuir expression, the theoretical monolayer capacity (q_0) is calculated from isotherm data and is a representation of the capacity of the sites in the substrate for adsorption of discrete sorbate molecules without any sorbate aggregation or micellar formation. Fig. 6b shows q_0 of cellulose II fibres treated with varying concentrations of NaOH, where it can be seen that q_0 increases with increasing NaOH concentration to a maxima at 3.33 mol dm^{-3} NaOH and then decreases with further increase in NaOH concentration to a plateau above 5.0 mol dm^{-3} NaOH; it can be concluded that the maximum number of available sites for adsorption are observed for cellulose II fibres treated with 3.33 mol dm^{-3} NaOH. This maximum may have been due to formation of the new available sites, and the plateau represents the fully swollen material. Fig. 6b demonstrates that the RSF trends for water sorption (Fink et al., 1986) also show similarity to theoretical monolayer capacity (q_0) of cellulose II fibres treated with varying concentrations of NaOH, concurring that accessibility to the AGU for sorption is concentration dependent.

Adsorption of dyes onto cellulosic fibres is typically associated with a Freundlich isotherm; sorption theory teaches that the interaction between dye molecules and cellulosic fibres is based on hydrogen bonding and van der Waals interactions (Shore, 1995). Isotherms plotted from the experimental data (Fig. 4) do not indicate limited adsorption (Langmuir isotherm); hence, it is possible that sorption observed herein may occur *via* a combination of Langmuir and Freundlich isotherms. The most intriguing aspect is the possibility of some site specificity, as indicated by the close correlation to the Langmuir isotherm, and the question arises as to how this occurs in a system theoretically based on non-site-specific interactions (Freundlich isotherm).

Carboxylic acid (COOH) groups are formed in cellulosic fibres through oxidation of glucose rings during processing operations such as bleaching or mercerizing (Nevell, 1995), and Stana-Kleinschek, Ribitsch, Kreze, and Fras (2002) suggested that these provide anionic sites for adsorption. Previous experimental studies have found that bleached, mercerized cotton fibre contains 1.9×10^{-5} mol carboxylic acid groups per g fibre (Blackburn et al., 2007); bleached lyocell fibre has a COOH content of 1.9×10^{-5} mol g^{-1}, decreasing to a minimum of 1.35×10^{-5} mol g^{-1} COOH when treated with 3.0 mol dm^{-3} NaOH obtained by 9*H*-fluoren-2-yl-diazomethane (FDAM) methods (Öztürk et al., 2009). Fig. 2b shows that hydrolyzed RR120 has several regions of strongly negative electrostatic potential, primarily due to the presence of six sulfonate groups ($-SO_3^-$) on the molecule. When electrolyte is added to the system (40 g dm^{-3} NaCl herein), Fig. 3b demonstrates that the carboxylate group ($-COO^-$) of the partially oxidized cellulose substrate associates with a Na^+ counterion, providing an intermediate or bridge function between substrate and sorbate, effectively creating a site with strongly positive electrostatic potential; negatively charged dye molecules can then adsorb *via* electrostatic interaction onto these positively charged sites in the fibre. However, if we consider hydrolyzed RR120 binding through an electrostatic mechanism in 1:1 stoichiometry with one carboxylate group ($-COO^-$) and a bridging Na^+ ion, it is clear that q_0 herein is significantly in excess of the number of available sites in the substrate, being 5.46×10^{-5} mol g^{-1} for lyocell treated with 0.0 mol dm^{-3} NaOH (*ca.* 3× [$-COO^-Na^+$] sites available), and 6.91×10^{-5} mol g^{-1} at 3.33 mol dm^{-3} NaOH (*ca.* 5.2× [$-COO^-Na^+$] sites available).

Clearly, sorption occurs in excess of experimentally determined q_0 as a result of non-site-specific interactions, more typical of a Freundlich isotherm. Hydrogen bonding and other short-range attractive forces can occur between the dye molecule and the glucose units of the heterogeneous polymer; Fig. 3a shows positive electrostatic potential in a non-oxidized glucose moiety, offering the opportunity for hydrogen bonding with electronegative moieties in the dye molecule. In addition, hydrogen bonds can form directly between hydroxyl groups in the cellulose II substrate and the extended π-electron system of the dye molecule (so-called Yoshida forces) (Yoshida, Osawa, & Oda, 1964); as Lewis (1998) observes, if π–π interactions are considered in the wider context of electrostatic interactions then the existence of π-facial hydrogen bonds between planar dye molecules (*e.g.* RR120) and cellulose substrates appears very likely. Moreover, aromatic residues in the dye are more likely to hydrogen bond with the cellulose –OH groups than hydrogen bond with themselves; this does not, of course, preclude π–π interactions as a strong association force.

Another parameter which was calculated from obtained results is adsorption energy (ΔG^0), also known as a standard free energy of dyeing or standard affinity of the dye for the substrate. ΔG^0 in systems where dye adsorbs onto cellulose II fibres has been related to the internal surface character of the substrate (Ibbett, Phillips, et al., 2006), and a higher value corresponds to more thermodynamically favourable dye sorption. For the Langmuir isotherm (which displays higher correlation), ΔG^0 increases with increasing NaOH concentration to a maxima between 2.53 and 3.33 mol dm^{-3} NaOH and then decreases with further increase in NaOH concentration to a plateau above 5.0 mol dm^{-3} NaOH (Fig. 7); it can be concluded that sorption of hydrolyzed reactive dyes onto cellulose II fibres is most thermodynamically favourable for substrates treated with 2.53–3.33 mol dm^{-3} NaOH.

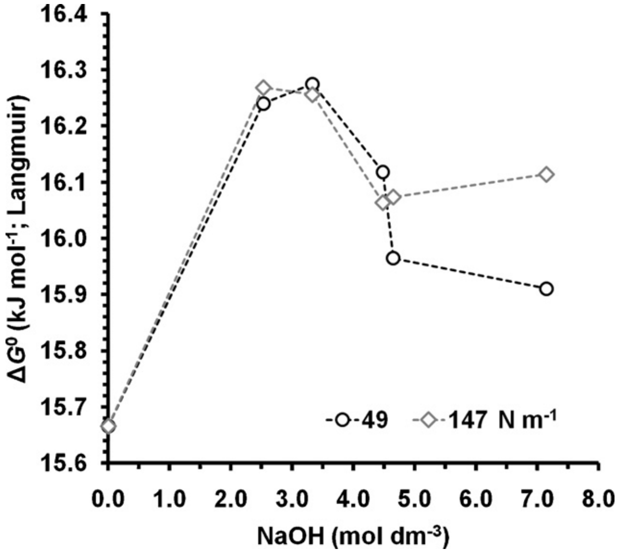


Fig. 7. Adsorption energy (ΔG^0) of cellulose II fibres treated with varying concentrations of NaOH, under applied tension of 49 N m^{-1} and 147 N m^{-1}, as observed when applied to Langmuir isotherm.

However, when fitting the data to the Freundlich isotherm there is not such an obvious increase in ΔG^0 with increasing NaOH concentration and values are relatively consistent across the concentration ranges applied. This observation does not devalue those for the Langmuir isotherm and actually raises the issue worthy of investigation that some site-specific sorption is occurring at some level within the fibre, hence the unexpected correlation to the Langmuir isotherm.

Blackburn et al. (2007) demonstrated that in cellulosic fibres the fibre surface exists as a layer of fibrils and microfibrils through which liquid can flow and as their state in water changes from solid phase, through a gel phase, to a solution phase as fibrils have heterogeneity all the way down to molecular dimensions. Below the fibrillar layer exists a pore network within the main bulk of the fibre through which liquid flow also occurs. For cellulose I fibres, fibrillar layer void spaces as large as 100 μm may be expected, and in the bulk of the fibre pore sizes range from 10 to 300 Å in diameter, hence, molecular size of the sorbate is an important factor in adsorption. Current knowledge of alkali treatment suggests that increasing treatment concentration of alkali causes strong lateral fibre swelling and subsequently increases accessible internal volume within the structure of the fibre (Colom & Carrillo, 2002; Ibbett & Hsieh, 2001; Ibbett, Phillips, et al., 2006; Široký et al., 2010). The observed differences in sorption could be explained by the accessible pore volume (APV) of lyocell fibres to probes as a function of NaOH concentration. Öztürk et al. (2009) used inversion size exclusion chromatography (ISEC) in combination with molecular probes up to 35 Å in diameter to assess the APV of lyocell fibres treated with aqueous NaOH solutions (up to 8 mol dm^{-3} NaOH). It was demonstrated that the upper limit of pore diameter in untreated and alkali treated lyocell was 27–32 Å, and it was additionally shown that for pore diameters of 19 Å and below that APV increased with increasing NaOH concentration to a maxima around 2.5 mol dm^{-3} NaOH and then decreased with further increase in NaOH concentration to a plateau above 4.0–5.0 mol dm^{-3} NaOH; in general APV at 2.5 mol dm^{-3} NaOH was *ca.* 10% higher than for untreated lyocell.

From molecular dynamic calculations (Fig. 2a), it is observed that the dimensions of hydrolyzed RR120 are about 30 Å (length) × 14 Å (wide) × 3.5 Å (depth) in one of the minimum energy states, providing a molecular diameter of 14 Å (end-on). As the diameter of hydrolyzed RR120 is <19 Å, it seems likely that the maximum APV at around 2.5 mol dm^{-3} NaOH observed by Öztürk et al. (2009) influences the accompanying maxima in q_0 and ΔG^0, which was indeed observed from the experimental results obtained herein. Hence, maximum q_e, q_0 and ΔG^0 are observed for cellulose II fibre treated with 2.53–3.33 mol dm^{-3} NaOH as this concentration range affects the greatest increase in APV.

5. Conclusions

It is observed that greatest adsorption of dye onto the substrate at equilibrium (q_e) occurs for cellulose II fibres treated with 2.53 and 3.33 mol dm^{-3} aqueous NaOH solution. Correlation to sorption isotherms is most closely associated with a Langmuir type isotherm, indicating limited, site-specific adsorption, however, correlation to the Freundlich isotherm is still significant, typical of unlimited adsorption at non-specific sites, hence, sorption observed potentially occurs *via* a combination of Langmuir and Freundlich isotherms.

For the Langmuir expression, the theoretical monolayer capacity (q_0) increases with increasing NaOH concentration to a maxima at 3.33 mol dm^{-3} NaOH and then decreases with further increase in NaOH concentration to a plateau above 5.0 mol dm^{-3} NaOH; it can be concluded that the maximum number of available sites for adsorption are observed for cellulose II fibres treated with 3.33 mol dm^{-3} NaOH.

It is suggested that when electrolyte is added to the system carboxylate groups ($-COO^-$) of the partially oxidized cellulose substrate associates with a Na^+ counterion effectively creating a site with strongly positive electrostatic potential for sorption of negatively charged dye molecules *via* electrostatic interaction. However, it is clear that q_0 herein is significantly in excess of the number of available sites in the substrate, hence, sorption occurs in excess of experimentally determined q_0 as a result of non-site-specific interactions, more typical of a Freundlich isotherm.

Adsorption energy (ΔG^0), as calculated from the Langmuir isotherm, increases with increasing NaOH concentration to a maxima between 2.53 and 3.33 mol dm^{-3} NaOH and then decreases with further increase in NaOH concentration to a plateau above 5.0 mol dm^{-3} NaOH and it is demonstrated that sorption of hydrolyzed reactive dyes onto cellulose II fibres is most thermodynamically favourable for substrates treated with 2.53–3.33 mol dm^{-3} NaOH. Although the Langmuir isotherm correlates most significantly with the data obtained, very close correlation with the Freundlich isotherm is also observed. It is proposed that sorption occurs *via* a combination of both theoretical models: sorption displays features expected for a cellulosic substrate, occurring through hydrogen-bonding and van der Waals interactions (typical for Freundlich isotherms); however, significant correlation with the Langmuir isotherm indicates that some site-specific sorption is occurring within these alkali treated cellulose II substrates, and it is proposed that carboxylate functions in the polymer may provide these sites.

Applying the work of Öztürk et al. (2009) concerning accessible pore volume (APV) of lyocell fibres, it is concluded that pores in the fibre significantly affected by alkali treatment (<20 Å diameter) and the accessibility of dye (14 Å) sorption into those pores accounts the differences observed herein; maximum q_e, q_0 and ΔG^0 are observed for cellulose II fibre treated with 2.53–3.33 mol dm^{-3} NaOH as this concentration range affects the greatest increase in APV.

Acknowledgments

The authors thank The University of Leeds and Lenzing AG for the provision of a scholarship to Mr. Široký. The authors would also like to acknowledge the assistance of Dr. Parikshit Goswami, Dr. Barbora Široká and Dr. Avinash Manian for help with the experimental work and also for fruitful discussion of the results.

References

Albrecht, W., Reintjes, M., & Wulfhorst, B. (1997). Lyocell fibres. *Chemical Fibers International*, *47*, 298–304.

Blackburn, R. S., Harvey, A., Kettle, L. L., Manian, A. P., Payne, J. D., & Russell, S. J. (2007). Sorption of chlorhexidine on cellulose: Mechanism of binding and molecular recognition. *Journal of Physical Chemistry B*, *111*, 8775–8784.

Blackburn, R. S., Harvey, A., Kettle, L. L., Payne, J. D., & Russell, S. J. (2006). Sorption of poly(hexamethylenebiguanide) on cellulose: Mechanism of binding and molecular recognition. *Langmuir*, *22*, 5636–5644.

Bredereck, K., & Hermanutz, F. (2005). Man-made cellulosics. *Review of Progress in Coloration and Related Topics*, *35*, 59–75.

Carrillo, F., Lis, M. J., & Valldeperas, J. (2002). Sorption isotherms and behaviour of direct dyes on lyocell fibres. *Dyes and Pigments*, *53*, 129–136.

Colom, X., & Carrillo, F. (2002). Crystallinity changes in lyocell and viscose-type fibres by caustic treatment. *European Polymer Journal*, *38*, 2225–2230.

Connolly, M. L. (1983). Analytical molecular-surface calculation. *Journal of Applied Crystallography*, *16*, 548–558.

Fink, H. P., Dautzenberg, H., Kunze, J., & Philipp, B. (1986). The composition of alkali cellulose – A new concept. *Polymer*, *27*, 944–948.

Freundlich, H. (1906). Concerning adsorption in solutions. *Zeitschrift für Physikalische Chemie*, *57*, 385–470.

Gessler, K., Krauss, N., Steiner, T., Betzl, C., Sarko, A., & Saenger, W. (1995). β-D-Cellotetraose hemihydrate as a structural model for cellulose. 2. An X-ray diffraction study. *Journal of the American Chemical Society*, *117*, 11397–11406.

Goswami, P., Blackburn, R. S., El-Dessouky, H. M., Taylor, J., & White, P. (2009). Effect of sodium hydroxide pre-treatment on the optical and structural properties of lyocell. *European Polymer Journal*, *45*, 455–465.

Heinze, T., & Pfeiffer, K. (1999). Studies on the synthesis and characterization of carboxymethylcellulose. *Angewandte Makromolekulare Chemie*, *266*, 37–45.

Heinze, U., & Wagenknecht, W. (1998). *Comprehensive cellulose chemistry. Functionalisation of cellulose*. Weinheim: Wiley-VCH.

Holme, I. (1976). Fibre physics and chemistry in relation to coloration. *Review of Progress in Coloration and Related Topics*, *7*, 1–22.

Hosemann, R. (1950). Der ideale parakristall und die von ihm gestreute koharente röntgenstrahlung. *Zeitschrift Fur Physik*, *128*, 465–492.

Hosemann, R., Willmann, G., & Roessler, B. (1972). Paracrystalline structure of molten metals. *Physical Review A*, *6*, 2243–2247.

Ibbett, R. N., & Hsieh, Y.-L. (2001). Effect of fibre swelling on the structure of lyocell fabrics. *Textile Research Journal*, *71*, 164–173.

Ibbett, R. N., Kaenthong, S., Phillips, D. A. S., & Wilding, M. A. (2006). Characterisation of the porosity of regenerated cellulosic fibres using classical dye adsorption techniques. *Lenzinger Berichte*, *85*, 77–86.

Ibbett, R. N., Phillips, D. A. S., & Kaenthong, S. (2006). Evaluation of a dye isotherm method for characterisation of the wet-state structure and properties of lyocell fibre. *Dyes and Pigments*, *71*, 168–177.

Inglesby, M. K., & Zeronian, S. H. (2002). Direct dyes as molecular sensors to characterize cellulose substrates. *Cellulose*, *9*, 19–29.

Kim, Y., Kim, C., Choi, I., Rengraj, S., & Yi, J. (2004). Characterisation of the porosity of regenerated cellulosic fibres using classical dye adsorption techniques. *Environmental Science and Technology*, *38*, 924–931.

Klemm, D., Heublein, B., Fink, H. P., & Bohn, A. (2005). Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie-International Edition*, *44*, 3358–3393.

Kolpak, F. J., & Blackwell, J. (1976). Determination of structure of cellulose II. *Macromolecules*, *9*, 273–278.

Kono, H., & Numata, Y. (2004). Two-dimensional spin-exchange solid-state NMR study of the crystal structure of cellulose II. *Polymer*, *45*, 4541–4547.

Kreze, T., & Malej, S. (2003). Structural characteristics of new and conventional regenerated cellulosic fibres. *Textile Research Journal*, *73*, 675–684.

Langan, P., Nishiyama, Y., & Chanzy, H. (1999). A revised structure and hydrogen-bonding system in cellulose II from a neutron fibre diffraction analysis. *Journal of the American Chemical Society*, *121*, 9940–9946.

Langmuir, I. (1916). The constitution and fundamental properties of solids and liquids. Part I. Solids. *Journal of the American Chemical Society*, *38*, 2221–2295.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, *40*, 1361–1403.

Lewis, D. M. (1998). Dyestuff-fibre interactions. *Review of Progress in Coloration and Related Topics*, *28*, 12–17.

Luo, M., Zhang, X. L., & Chen, S. L. (2003). Enhancing the wash fastness of dyeings by a sol–gel process. Part 1. Direct dyes on cotton. *Color Technology*, *119*, 297–300.

Nevell, T. P. (1995). Cellulose: Structure, properties and behaviour in the dyeing process. In J. Shore (Ed.), *Cellulosics Dyeing*. Bradford: Society of Dyers and Colourists.

Okano, T., & Sarko, A. (1984). Mercerization of Cellulose. 1. X-ray-diffraction evidence for intermediate structures. *Journal of Applied Polymer Science*, *29*, 4175–4182.

Okano, T., & Sarko, A. (1985). Mercerization of cellulose. 2. Alkali cellulose intermediates and a possible mercerization mechanism. *Journal of Applied Polymer Science*, *30*, 325–332.

Öztürk, H. B., Potthast, A., Rosenau, T., Abu-Rous, M., MacNaughtan, B., Schuster, K. C., et al. (2009). Changes in the intra- and inter-fibrillar structure of lyocell (TENCEL®) fibres caused by NaOH treatment. *Cellulose*, *16*, 37–52.

Peters, R. H., & Ingamells, W. (1973). Theoretical Aspects of Role of Fiber Structure in Dyeing. *Journal of the Society of Dyers and Colourists*, *89*, 397–405.

Raymond, S., Heyraud, A., Tran Qui, D., Kvick, A., & Chanzy, H. (1995). Crystal and molecular-structure of β-D-cellotetraose hemihydrate as model of cellulose II. *Macromolecules*, *28*, 2096–2100.

Roessler, A., & Jin, X. N. (2003). State of the art technologies and new electrochemical methods for the reduction of vat dyes. *Dyes and Pigments*, *59*, 223–235.

Shore, J. (1995). Dyeing with reactive dyes. In J. Shore (Ed.), *Cellulosics dyeing*. Bradford: Society of Dyers and Colourists.

Široký, J., Blackburn, R. S., Bechtold, T., Taylor, J., & White, P. (2010). Attenuated total reflectance Fourier-transform infrared spectroscopy analysis of crystallinity changes in lyocell following continuous treatment with sodium hydroxide. *Cellulose*, *17*, 103–115.

Široký, J., Manian, A. P., Široká, B., Abu-Rous, M., Schlangen, J., Blackburn, R. S., et al. (2009). Alkali treatments of lyocell in continuous processes. I. Effects of temperature and alkali concentration on the treatments of plain woven fabrics. *Journal of Applied Polymer Science*, *113*, 3646–3655.

Stana-Kleinschek, K., Ribitsch, V., Kreze, T., & Fras, L. (2002). Determination of the adsorption character of cellulose fibres using surface tension and surface charge. *Materials Research Innovations*, *6*, 13–18.

Voyles, P. M., Zotov, N., Nakhmanson, S. M., Drabold, D. A., Gibson, J. M., Treacy, M. M. J., et al. (2001). Structure and physical properties of paracrystalline atomistic models of amorphous silicon. *Journal of Applied Physics*, *90*, 4437–4451.

Wang, Q., & Hauser, P. J. (2009). New characterization of layer-by-layer self-assembly deposition of polyelectrolytes on cotton fabric. *Cellulose*, *16*, 1123–1131.

White, P., Hayhurst, M., Taylor, J., & Slater, A. (2005). Lyocell fibres. In R. S. Blackburn (Ed.), *Biodegradable and sustainable fibres*. Cambridge: Woodhead Publishing Limited.

Yoshida, Z., Osawa, F., & Oda, R. (1964). Intermolecular hydrogen bond involving a π-base as the proton acceptor. I. Detection by the refractive index method. *Journal of Physical Chemistry*, *68*, 2895–2898.

Zhou, L. M., Yeung, K. W., Yuen, C. W. M., & Zhou, X. (2003). Effect of mercerisation and crosslinking on the dyeing properties of ramie fabric. *Color Technology*, *119*, 170–176.

Zhu, Y., Ren, X., & Wu, C. (2004). Influence of alkali treatment on the structure of newcell fibres. *Journal of Applied Polymer Science*, *93*, 1731–1735.