

The Adsorption Mechanism of Water-based Ink Particles onto Cellulosic Fibers

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Water-based flexographic-printed ink has attracted much attention due to the reduced emission of volatile organic compounds in the printing process. However, it is difficult to remove water-based ink particles with small particle size and high hydrophilicity because they are easily reabsorbed onto cellulosic fibers during wastepaper recycling. In this paper, the adsorption mechanism of water-based ink particles onto fibers was studied by using isotherm models and adsorption dynamic kinetics models at different temperatures. The adsorption process was fitted to the Freundlich isotherm, and the adsorption behavior was spontaneous and exothermic processes with an increase of entropy. It fitted well with the pseudo-second-order rate model, and the equilibrium adsorption amounts at three temperature conditions were 2.55, 2.34, and 2.21 mg/g, respectively. The B value was $9.20 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$, and the E_a value was $15.6 \text{ kJ}\cdot\text{mol}^{-1}$. The results showed that it was easier to remove the water-based ink particles from cellulosic fibers under shorter contact time and higher operation temperature during wastepaper recycling. It would be helpful to optimize the wastepaper recycling operation and to develop a novel deinking process.

Keywords: Water-based ink; Cellulosic fibers; Adsorption kinetics; Adsorption isotherms

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INTRODUCTION

Wastepaper recycling reduces the consumption of natural plant resources in the paper industry, and it is beneficial to alleviate environmental pressures. Recycled fibers make up one third of the paper-based fibers globally (Xiang *et al.* 2019). The huge challenge for extensive use of recycled fibers is to develop high-efficiency ink removal processes. Generally, the efficiency of ink removal is determined by the species of fibers, inks, and printing processes (Tsatsis *et al.* 2017). Compared with oil-based ink, water-based ink is welcomed in the printing and packaging industries. However, as little as 5% flexographic newsprints paper in a recycling furnish can significantly reduce the brightness of secondary fibers (Larson 1997). In addition, it is difficult for water-based ink printed paper or paperboard to be deinked by the traditional flotation process due to the small particle size and high hydrophilicity of water-based ink particles. The presence of water-based ink particles seriously affects the optical property of the recycled fibers.

Water-based ink is characterized by using water as the medium or major liquid component in which most of additives are dissolved or suspended. In general, water-based ink contains the carboxylated polymer and free alkali, such as ammonia hydroxide, which is used to dissolve the resin (Fillat *et al.* 2015). In the water-based ink printing process, the

pH is gradually reduced due to the base vaporization, which results in the desolubilization of polymers to improve the attachment of pigments to the substrate. Under high pH conditions in wastepaper recycling, the carboxylated polymer is soluble and the binders of water-based ink are dissolved continually; concurrently, the size of ink particles decreases significantly (Lee *et al.* 2013). Due to the small particle size (0.1 to 1 μm) and hydrophilic properties of water-based ink particles (Kemppainen *et al.* 2011), it is difficult to remove them from fibers, and they tend to reabsorb on the fiber surface or to deposit inside the lumen of fibers in the traditional flotation deinking process. The re-deposited ink is quite difficult to remove in the subsequent washing stages without substantial loss of fibers. Some additives in the water-based ink (such as surfactants and inorganic ions) and recycling conditions can decrease the reabsorption amount of water-based ink particles onto fibers (Gecol *et al.* 2004). The published research mainly focuses on the optimization of reabsorption process and related pulping parameters, but there has been a lack of published work on the adsorption mechanism of ink particles onto fibers.

In this work, the adsorption mechanism of water-based ink particles onto fibers was studied from the viewpoint of the adsorption isotherms, kinetics, and thermodynamics. Specially, the adsorption isotherm model of water-based ink particles onto cellulosic fibers was investigated by varying the contact time and temperature in the adsorption process to determine the adsorption capacity; the thermodynamic model was used to explore the adsorption possibility and the adsorption degree of water-based ink particles onto fibers; the kinetics model was applied to clarify the effect of contact time on the deposition of water-based ink particles onto fibers. The main objective of this study was to schematically investigate the adsorption mechanism of water-based ink particles onto fibers and to guide the water-based ink removal process in industrial processes.

EXPERIMENTAL

Materials

Water-based ink (Shanggu Caitong-TGS; black) was obtained from Tianjin Hanlin Tongshang Technology Co., Ltd. (Tianjin, China). The physicochemical properties of secondary fiber are hard to control due to different fiber types, additives, and seasonal variations in the fiber recovery system. Therefore, softwood bleached kraft pulp (SBKP) was chosen as the raw material in the adsorption simulation process in order to control the key parameters of the adsorption procedure and to simplify the fiber adsorption process.

Water-based Ink Aging

The water-based ink was aged before the adsorption experiment to simulate the maturation of water-based ink during the printing process. The water-based ink suspension, which included 18 wt% carbon black, 10 wt% polyacrylate, 5 wt% additives, and 67 wt% water, was aged at 105 °C for 8 h. As the size of most water-based ink particles in the flotation deinking process was less than 1 μm , the size distribution of the water-based ink particles was investigated by a Nano Brook Laser Particle Size Analyzer (Model 90 PLUS/BI, Brookhaven Instruments Co. Ltd., New York, USA). The grinded ink particles were dispersed in water and homogenized with a high-speed disperser to obtain a uniformly dispersed ink suspension.

Adsorption Procedure

The apparatus for the simulative adsorption experiment of ink particles onto fibers is illustrated in Fig.1. The apparatus consisted of a 500 mL beaker to hold the suspension of ink particles and testing fibers, a 200-mesh screening chamber to filter out fibers that interfere the concentration measurement of water-based ink particles, agitator, and magnetic stirring bar (the rotation speed was set at 600 rpm) to maintain the stable suspension state of the mixture. The suspension of ink particles and fibers was kept at 10, 20, or 30 °C. The concentration of the ink particles in the suspension before and after the adsorption process was determined by transferring 2.5 mL of filtrate in the screening chamber to the photometric detector for UV/Vis measurement. Based on the ink particle concentration in the suspension before and after the adsorption process, the adsorption capacity (q_e) of ink particles onto fibers was determined using Eq. 1,

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (1)$$

where C_0 and C_e ($\text{g}\cdot\text{L}^{-1}$) are the initial and equilibrium concentrations of water-based ink particles, V (L) is the volume of the mixing suspension, and m (g) is the mass of fibers in the mixing suspension.

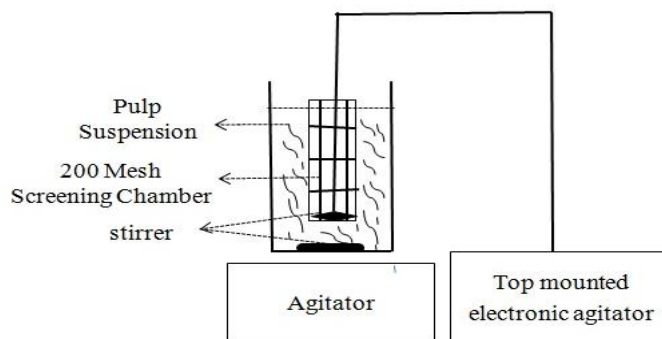


Fig. 1. The experimental apparatus for the adsorption of water-based ink particles onto fibers

Determination of Water-based Ink Particles Concentration

The maximal absorbing wavelength (λ_{max}) for the water-based ink particles was determined at 700 nm with a UV/Vis spectrometer (Model T6, Beijing General Analysis Instrument Co. Ltd., Beijing, China). A linear trend between the concentration of water-based ink particles in the suspension and the absorbance of water-based ink particles suggested that Beer-Lambert Law was applicable to water-based ink particles in the testing concentration range.

RESULTS AND DISCUSSION

Characterization of Water-based Ink Particles and Cellulosic Fibers

As shown in Fig. 2, the size distribution of the water-based ink particles ranged from 92 to 236 nm. Based on the previous research, the morphological properties of cellulosic fibers have significant impact on the adsorption and accumulation process of water-based ink particles onto cellulosic fibers, especially the pore morphology, such as pore shape, pore volume, and pore size distribution (Mahfoudhi and Boufi 2017). The pore size of SBKP fibers was divided into wide ranges, and the majority had relatively bigger pore volume (bigger than 100 nm).

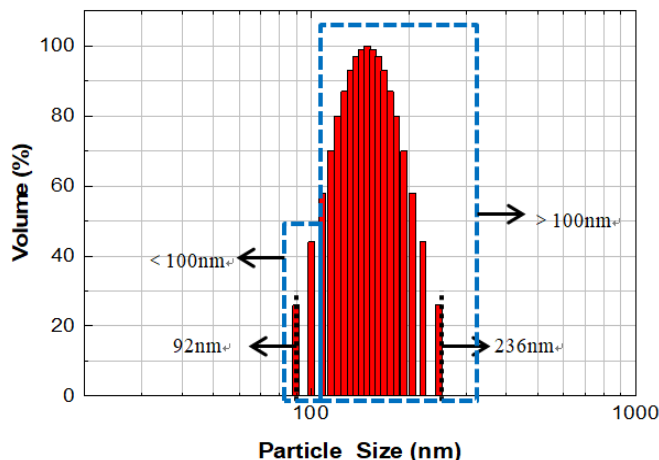


Fig. 2. The size distribution of the water-based ink particles after grinding treatment

Effect of Contact Time and Temperature on the Adsorption Process

In the adsorption process of water-based ink particles onto fibers, contact time and temperature can affect the adsorption behavior (including equilibrium time, adsorption rate, and equilibrium adsorption capacity) of the solid-solid interface (Fan *et al.* 2017). The effect of contact time (t) and temperature on the adsorption capacity (q_e) of water-based ink particles onto fibers are shown in Fig. 3.

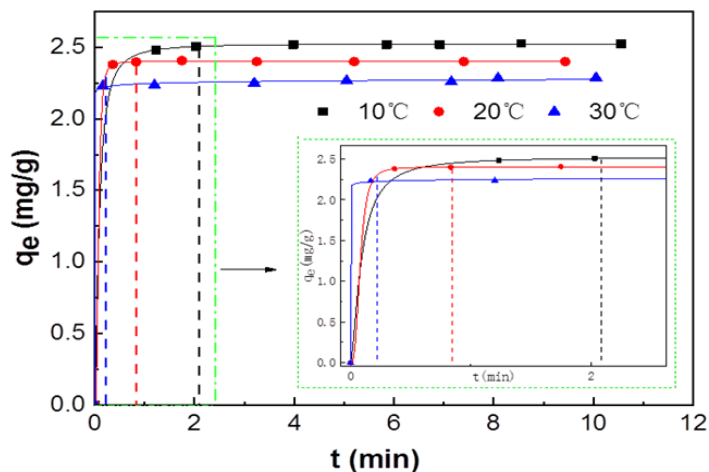


Fig. 3. Effect of contact time (t) and temperature on the adsorption capacity (q_e) of water-based ink particles onto fibers (Initial water-based ink concentration of 0.36g/L; the fiber content of 1%)

Figure 3 shows that at any temperature, the adsorption capacity of water-based ink particles onto fibers was dramatically increased at the very beginning of adsorption procedure and then reached the adsorption equilibrium with the increase of contact time. According to the adsorption curve in Fig. 3, the adsorption process could be divided into two phases: a rapid-adsorption phase and a slow-adsorption phase. The former indicated that the adsorption capacity of ink particles onto fibers dramatically increased with the contact time, and the latter showed that the adsorption capacity tended to stabilize. The rapid phase was due to easily available active adsorption sites on the fiber surface (Devi and Saroha 2016). As porous materials, fibers have many folds and pores on their surface that allow the adsorption/accumulation of ink particles, as shown in Figs. 4(a) and (c).

Moreover, there was a certain proportion of ink particles with small size (less than 100 nm), which could easily deposit onto the pores of fiber surface, as shown in Figs. 4(b) and (d) (Bhunia *et al.* 2013). The slow-adsorption phase represented the diffusion process, controlled by the ink particles concentration gradient between the fiber surface and the bulk suspension (Liu *et al.* 2014). Finally, the adsorption capacity did not change after the adsorption equilibrium was reached. Therefore, in an industrial deinking process, it is important to remove the ink within a short time to prevent the water-based ink particles from redepositing onto fibers.

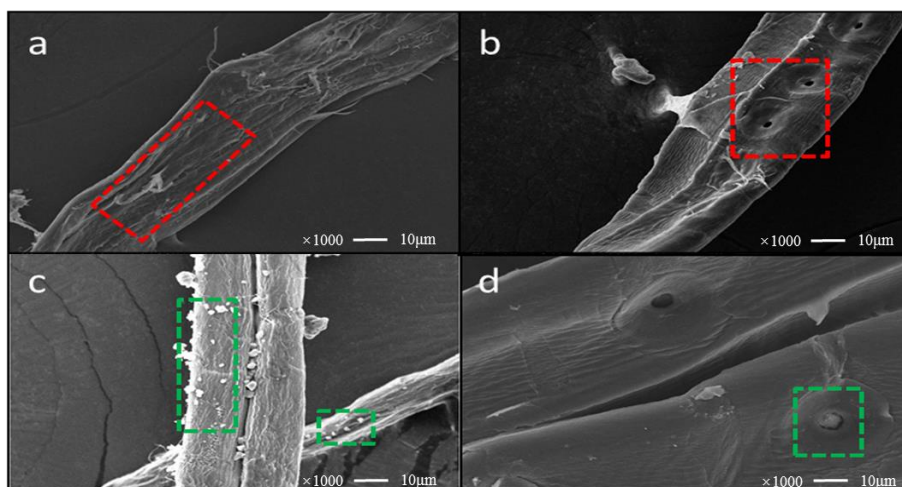


Fig. 4. SEM images for the water-based ink particles onto fibers

Figure 3 also shows that the adsorption rate increased with the increase of temperature, which was attributed to the increased diffusion rate of the water-based ink particles onto fibers. Under the temperature of 10, 20, and 30 °C, the adsorption amounts of water-based ink particles onto the fibers at equilibrium (q_e) were 2.55, 2.33, and 2.18 mg/g, respectively, indicating that the adsorption amounts of ink particles in fibers at equilibrium (q_e) decreased with the increase of temperature.

Adsorption Isotherms and Thermodynamic Analysis

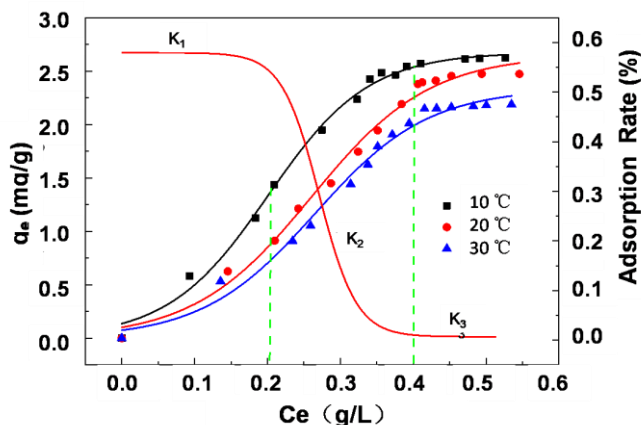


Fig. 5. The adsorption isotherms of water-based ink particles onto fiber surfaces (Initial water-based ink concentration of 0 to 0.6 mg/L; fibers content of 1%; contact time of 30 min)

Figure 5 shows the adsorption isotherms of water-based ink particles onto fibers under three temperatures (10, 20, and 30 °C). Based on the relationship between the absorption amount (q_e) of ink particles onto fiber surface and the residual amount of ink particles in aqueous phase (C_e), the development trend of adsorption rate (K) was studied with the increase of ink particle concentration. As shown in Fig. 5, the adsorption rate (K) decreased with increasing ink particle concentration (C_i). When C_i was smaller than 0.2 g/L, K was relatively bigger due to the larger concentration gradient of ink particles between the aqueous phase and fiber surface. With the increase of C_i , K gradually decreased due to the reduction of adsorption sites on the fiber surface. When C_i was higher than 0.4g/L, the adsorption sites on fiber surface were almost filled, so K was close to 0. It was evident that the fiber adsorption capacity increased with the increased concentration of ink particles in solution (Gobi *et al.* 2011). With the increase of initial concentration of ink particles, the adsorption sites on fiber surface were almost saturated, leading to less binding sites of ink particles on the fiber surfaces.

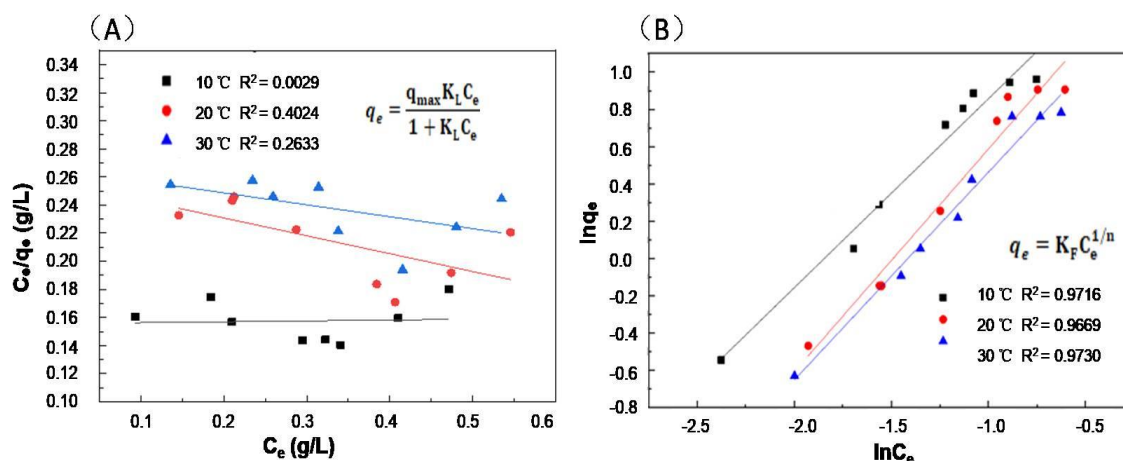


Fig. 6. Fitting results of the adsorption data for ink particles onto cellulosic fibers at varying experimental temperatures: (A) the adsorption experiment data were fitted with the Langmuir model, where the inset equation was the non-linear theoretical equation of the Langmuir isotherm model; (B) the adsorption experiment data were fitted with Freundlich isotherm model, where the inset equation was the non-linear theoretical equation of the Freundlich isotherm model.

The adsorption data for ink particles onto fibers was correlated with the Langmuir and Freundlich isotherm models. The fitting results are shown in Fig. 6. The numerical value of the determination coefficient R^2 was higher than 0.9 when the adsorption experiment data were fitted to the Freundlich isotherm model (Fig. 6(A)); meanwhile, the R^2 was much smaller than 0.5 when the adsorption experiment data were fitted to the Langmuir isotherm model (Fig. 6(B)). The fitting results indicated that the adsorption model of water-based ink particles onto fibers was fitted better to the Freundlich isotherm than to the Langmuir isotherm. According to the fitting curve, the $1/n$ and $\ln K_F$ of the Freundlich isotherm model were determined, which were calculated from the slope and intercept of the fitting curve, respectively. The K_F defines the adsorption capacities of the water-based ink particles onto fibers. The larger K_F indicates greater adsorption per unit mass of adsorbent. The K_F values at 10, 20, and 30 °C in Table 1 were 6.50, 5.95, and 4.85, respectively, indicating that the adsorption amounts of water-based ink particles onto fibers decreased with increased temperature. The value of $1/n$ is the empirical parameter for Freundlich equation. Generally, the adsorption process can be performed easily when $1/n$ is 0.1 to 1.0; it is difficult for it to occur when $1/n$ is more than 2. As shown in Table 1, the

$1/n$ value of the studied adsorption process was approximately 1, suggesting that it was easy for the water-based ink particles to deposit onto fiber surfaces. The isotherm constants of Freundlich isotherm model obtained from the fitting results are summarized in Table 1.

As the adsorption data were fitted better to the Freundlich isotherm model, the thermodynamic parameters for the adsorption process were obtained by plotting $\ln K_F$ against $1/T$ according to the Van't Hoff equation (Eq. 2),

$$\ln K_F = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (2)$$

where R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), T is the absolute temperature (K), and ΔH and ΔS are enthalpy ($\text{kJ}\cdot\text{mol}^{-1}$) and entropy changes ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) of the adsorption process, respectively, which can be calculated from the slope and intercept of the fitting curve. The free energy (ΔG) of the adsorption process was obtained from the difference ($\Delta H - T\Delta S$). As shown in Table 1, the negative ΔH ($-10.39 \text{ kJ}\cdot\text{mol}^{-1}$) value indicated the exothermic nature of the adsorption process. The ΔS ($12.67 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} > 0$) value showed that the adsorption entropy increased in the process, suggesting that there were strong affinity between fibers and water-based ink particles. The adsorption process was spontaneous because all the ΔG values were less than zero. Therefore, the low adsorption temperature is benefit to the adsorption process.

Table 1. Isotherm Constants of Freundlich and Thermodynamic Parameters for the Adsorption of Water-based Ink Particles onto Fibers at Different Temperatures

T (°C)	K_F	$1/n$	R^2	ΔH ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔS ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)	ΔG ($\text{kJ}\cdot\text{mol}^{-1}$)
10	6.50	1.01	0.9716	-10.39	12.67	-13.97
20	5.95	1.19	0.9669	-10.39	12.67	-14.10
30	4.85	1.11	0.9730	-10.39	12.67	-14.22

Adsorption Kinetics

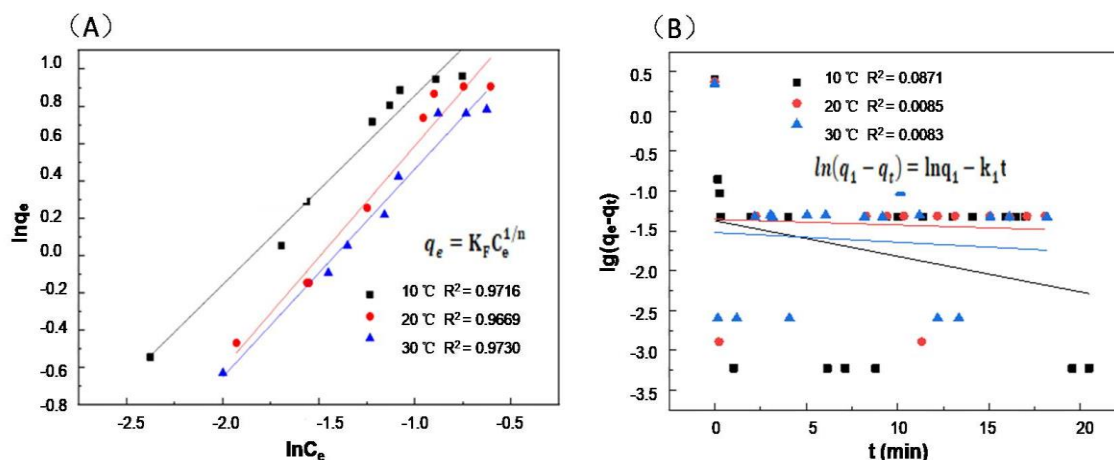


Fig. 7. Adsorption kinetic process of water-based ink particles onto fibers: (A) the fitting results of the experimental data based on the Lagergren's first-order rate model, the insert equation was the Lagergren's first-order rate equation; (B) the fitting results of the experiment data based on the pseudo-second-order rate model, the insert equation was the Ho's second-order rate equation.

The pseudo-first-order and pseudo-second-order rate equations were employed to interpret the experimental data. As shown in Fig. 7, the coefficient R^2 of the fitting equation based on Lagergren's first-order rate model was much smaller than 0.1 (Fig. 7(A)); meanwhile, the coefficient R^2 of the fitting equation based on the Ho's second-order rate model was 0.999 and very close to 1 (Fig. 7(B)). Based on the coefficients, the Ho's second-order rate equation was more suitable to describe the adsorbing kinetic process of water-based ink particles onto fiber, and the related kinetic parameters at 10, 20, and 30 °C are given in Table 2. The value of k_2 increased with the increase of temperature, suggesting that the diffusion rate of water-based ink particles was greater in high temperature; q_e decreased with the increase of temperature because the desorption rate was faster than the adsorption rate at a higher temperature.

Table 2. Kinetic Parameters for the Adsorption Process of Water-Based Ink Particles onto Fibers at 10, 20, and 30 °C

$T(^{\circ}\text{C})$	k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	q_e ($\text{mg}\cdot\text{g}^{-1}$)	R^2
10	13.37	2.55	0.999
20	17.23	2.34	0.999
30	20.68	2.21	0.999

The values of k_2 at different temperatures were treated with the Arrhenius equation as Eq. 3,

$$\ln k_2 = B - \frac{E_a}{RT} \quad (3)$$

where B is the frequency of adsorption ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$), E_a is the activation energy of reaction ($\text{kJ}\cdot\text{mol}^{-1}$), R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), and T is the absolute temperature.

The values of $\ln k_2$ was plotted against the reciprocal of absolute temperature ($1/T$) to determine the corresponding B and E_a from the intercept and the slope of regression line, respectively. The B was $9.20 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ and the E_a was $15.60 \text{ kJ}\cdot\text{mol}^{-1}$. Generally, sorption processes governed by an activation energy have energies greater than 25 to 30 $\text{kJ}\cdot\text{mol}^{-1}$; sorption processes governed by diffusion have energies less than 25 to 30 $\text{kJ}\cdot\text{mol}^{-1}$ (Ho *et al.* 2000). The E_a value of the adsorption process was less than 30 $\text{kJ}\cdot\text{mol}^{-1}$, indicating that diffusion behavior also happened in the adsorption process.

CONCLUSIONS

1. The adsorption capacity of water-based ink particles onto cellulosic fibers decreased with increasing temperature, and the adsorption amount increased with increased contact time. Adsorption isotherms indicated that the adsorption behavior of water-based ink particles onto cellulosic fibers was more fitted with the Freundlich isotherm model than the Langmuir isotherm model. In addition, a thermodynamic study revealed that the absorption process between water-based ink particles and cellulosic fibers was a spontaneous and exothermic process.
2. The kinetic study suggested that the adsorption process of water-based ink particles onto cellulosic fibers fitted very well with the pseudo-second-order kinetic model over a temperature range. The activation energy (E_a) of the sorption process was 15.6 $\text{kJ}\cdot\text{mol}^{-1}$, and the diffusion behavior also happened in the adsorption process.

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