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Valorization of human hair as methylene blue dye adsorbents

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Abstract: The present study was aimed at evaluating the performance of human hair as adsorbents for methylene blue (MB) dye removal. Human hair was treated using 0.1 M potassium hydroxide (KOH) and 0.1 M nitric acid, and the adsorbents were characterized for specific surface area and surface chemistry. The basic-treated human hair adsorbent (BH) exhibits a specific surface area of 3.51 m²/g, which is relatively higher than the acid-treated (AH) and untreated (UH) counterparts. The equilibrium data of all adsorbents obeyed the S-shaped isotherm, suggesting a cooperative adsorption. The BH displays a maximum capacity of 13.5 mg/g, while a comparable capacity of 3.4 mg/g was recorded by AH and UH. The adsorption of MB by BH increased with increasing pH. Based on the equilibrium and kinetics data, the adsorption of MB onto BH is proposed to have the following mechanisms: (i) external diffusion, (ii) intraparticle diffusion, and (iii) cooperative adsorption. In addition, the MB adsorption at a concentration of 20 mg/l is endothermic and spontaneous with temperature increasing from 35°C to 55°C. A basic treatment of human hair using KOH yields a promising adsorbent for dye in wastewater treatment.

Keywords: adsorbent; basic treatment; human hair; methylene blue (MB); S-shaped isotherm.

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List of abbreviations

AH	nitric acid-treated human hair adsorbent
BH	potassium hydroxide-treated human hair adsorbent
EDS	energy dispersive spectrometry
HCl	hydrochloric acid
HNO ₃	nitric acid
H ₂ SO ₄	sulfuric acid
KOH	potassium hydroxide
MB	methylene blue
MS	Microsoft
NaOH	sodium hydroxide
pH	potential of hydrogen
pI	isoelectric point
R ²	coefficient of determination
SSE	sum of squared error
UH	untreated human hair adsorbent

List of symbols

b	adsorption affinity (l/mg)
C	intercept of the intraparticle diffusion model (mg/g)
C_0	initial concentration (mg/l)
C_e	equilibrium concentration (mg/l)
$C_{e,a}$	amount of dye adsorbed (mg/l)
C_t	concentration at time t (mg/l)
dC_t/dt	gradient of concentration with time (mg/l · h)
K	equilibrium constant
K_p	the intraparticle diffusion rate constant (mg/g · h ^{0.5})
k_s	the S-shaped kinetics rate constant (h ⁻¹)
k_1	the pseudo-first-order rate constant (h ⁻¹)
k_2	the pseudo-second-order rate constant (g/mg · h)
m	mass of the adsorbent (g)
m_e	midpoint equilibrium concentration (mg/l)
m_t	midpoint of time (h)
Q_m	maximum adsorption capacity (mg/g)
q_e	equilibrium adsorption (mg/g)
q	adsorption at time t (mg/g)
R	the gas constant (8.314 J/mol · K)
T	temperature (K)
t	time (h)
V	volume of the solution (l)
ΔG	Gibbs free energy (J/mol)
ΔH	enthalpy (J/mol)
ΔS	entropy (J/mol · K)
π	delocalized π -electrons
–COOH	carboxylic group
–NH	amine group
–NH ₂	amino group

–OH phenolic group
 =O lactonic group
 –S–S– disulfide bond.

1 Introduction

There is a growing concern over the abundance of human hair waste in landfills that sometimes choke and disrupt the drainage system. Human hair is a biological waste with slow degradation rate. During the stages of natural decomposition, it releases ammonia and nitrogen. On the other hand, direct burning of human hair produces toxic gases such as ammonia, hydrogen sulfide, sulfur dioxide, and other volatiles like phenols, nitriles, pyrroles, and pyridines that bring about foul odor [1]. Because human hair waste can become a threat to the environment, an alternative solution to waste disposal is, therefore, imperative to be sought.

Human hair contains up to 95% protein that is mainly composed of polymers of amino acids such as keratin and cystine [2]. Keratin gives hair the strength, flexibility, durability, and functionality. Hydrogen bonds between the carboxylic (–CO–OH) and amine (–NH) groups provide stabilization to the hair structures [3]. These functional groups could also act as active sites for the removal of water pollutants through coordination mechanism and electrostatic attraction [4, 5]. Human hair is one of the highest nitrogen-containing organic materials, and some has been commercially converted into fertilizer [1]. Human hair is known for its unique properties, i.e. high tensile strength, slow degradation rate, scaly surface, thermal insulation, and interactions with water and oils [1]. In view of these traits, human hair can be considered as an excellent candidate of natural adsorbent for water pollutants removal [4, 6].

Human hair has high affinity for oils, and can attract certain chemical compounds from the solution. Ifelebuegu et al. [7] reported the adsorption of 9300 mg/g vegetable oil by detergent-washed human hair. Mahdavian [8] reported the removal of 33 mg/g lead(II) using NaOH-treated human hair. Human hair was also used for the removal of basic (cationic) dyes [9, 10]. Hashem et al. [9] reported a 16.9 mg/g removal of basic blue 69 by the untreated human hair. In general, the adsorption of heavy metals and cationic dyes onto hair-based adsorbent involves the interaction with the unpaired electrons in the nitrogen and oxygen atoms, by which the electrochemical bonds are formed between the oppositely charged substances [5, 11]. Specifically, the presence of amino and hydroxyl groups offers natural negative charges on

the hair surface for the adsorption of positively charged pollutants.

Dyes are often manufactured using chemicals that are highly toxic [12]. Methylene blue (MB) is a commonly used basic dye in textile industry because of its bright color and high intensity. It is very soluble in water, and highly visible even in trace amount [12]. The presence of dye in water bodies disrupts the penetration of sunlight, retards the photosynthesis process, thus decreasing the oxygen solubility, and consequently upsetting the aquatic ecosystem. Excessive exposure to MB can cause serious health problems such as increased heart rate, vomiting, jaundice, shock, Heinz body formation, quadriplegia, cyanosis, and tissue necrosis [12, 13]. Dye is purposely designed to withstand the chemical and microbial attacks, hence its removal from water has become a challenging task [14].

A number of natural materials have been tested as MB adsorbents. These include *Aleurites moluccana* seed [15], NaOH-treated orange peel [16], *Prosopis sicigera* L. wood [17], H₂SO₄-treated *Areca triandra* palm shell [18], chemically treated human hair [9], NaOH-treated pine nut shell [19], and chemically modified *Cocos nucifera* L. [20]. To the best of our knowledge, the adsorptive properties of the basic-treated human hair for dye removal are still not available in much of the published literature. To narrow down the gap, the present work was aimed to challenge the MB adsorption by three human hair-based adsorbents, namely untreated, acid-treated, and basic-treated. Potassium hydroxide (KOH) and nitric acid (HNO₃) were used in the treatment of human hair. The removal performance was evaluated based on the dye concentration, solution pH, contact time, and temperature. The findings were discussed and the removal mechanisms were proposed.

2 Materials and methods

Human hair residue was obtained from local hair salon located at the Johor state of Malaysia. All chemicals used (MB dye, KOH, sodium hydroxide, hydrochloric acid, and HNO₃) were of analytical-grade reagents.

2.1 Preparation and characterization of human hair adsorbents

Human hair was cut to a size of approximately 2 cm. Then it was soaked in distilled water, and boiled for 15 min to remove impurities. This step was repeated until the washed water becomes clear. Then the sample was oven-dried at 110°C for 24 h. After that, the dried sample was immersed in 0.1 M HNO₃ for 24 h, and then it was washed repeatedly using hot water until there is no further change in the

solution pH. Similar step was repeated for the basic-treated human hair adsorbent using 0.1 M KOH. No noticeable change in the shape or form of human hair was observed upon the treatment strategies. The three adsorbents, i.e. untreated, acid-treated, and basic-treated were designated as UH, AH and BH, respectively. All adsorbents were dried prior to use.

Human hair was characterized for its thermal behavior using a Perkin-Elmer thermogravimetric analyzer (TGA 7). The measurement was carried out under a nitrogen flow of 20 ml/min at a heating rate of 10°C/min. All adsorbents were analyzed for specific surface area, surface functional groups, and elemental composition. The measurement of single-point specific surface area was performed by Brunauer-Emmett-Teller method using a Micromeritics surface analyzer (Gemini 2360). The presence of surface functional groups was determined using a Shimadzu spectrometer (IRTracer-100). The energy dispersive spectrometry (EDS) was performed to obtain the elemental composition of human hair using a Hitachi field emission scanning electron microscope coupled with an EDS detector (SU8020). The measurements were performed twice and the average data were reported.

2.2 Adsorption studies

Thirty milligrams of the adsorbent was added in a series of conical flasks containing 30 ml of MB solution with concentrations between 2 and 50 mg/l. The solution pH was not adjusted, and was measured as pH 5.7 ± 0.1 . The control solution was prepared for reference. The mixture was allowed to equilibrate at room temperature for 72 h. After that, the supernatant was taken out for concentration measurement using a Dynamica visible spectrophotometer (Halo Vis -10) at a wavelength of 564 nm. The calibration was determined as $\text{a.u.} = 0.0176 \times \text{concentration}$, with $R^2 = 0.991$ for MB concentrations between 2 and 25 mg/l. The capacity of adsorption at equilibrium, q_e (mg/g) was calculated as $q_e = (C_0 - C_e) \times (V/m)$, where C_0 and C_e (mg/l) are the initial concentration and concentration at equilibrium, respectively, m (g) is the adsorbent mass, and V (l) is the volume of solution. The removal efficiency (%) was calculated as $(C_0 - C_e) \times 100 / C_0$. The effect of concentration was used to screen the removal performance by the three adsorbents; the resulting data were used to select the one used for the subsequent parameters evaluation which is described as follows.

The effect of pH was evaluated at MB concentrations of 5 and 10 mg/l, in which the solution pH was adjusted between pH 2 and 10 using 0.1 M NaOH or 0.1 M HCl. The concentrations were selected based on the equilibrium curve that demonstrates appreciable adsorption affinity. The control solution with the same adjusted pH was prepared for reference. The mixture was allowed to reach the equilibrium for 72 h, after which the concentration and pH at the equilibrium were measured.

Three concentrations were selected for the rate of adsorption and the effect of temperature based on appreciable adsorption affinity and maximum capacity. Thirty milligrams of human hair adsorbent was brought into intimate contact with a series of 30 ml MB solution of known concentrations. The supernatant was withdrawn from the solution at the preset time intervals for the concentration measurement. The adsorption capacity at time t , q_t was calculated as $q_t = (C_0 - C_t) \times (V/m)$, where C_t (mg/l) is the measured MB concentration at time t . The adsorption of MB at varying temperatures was performed by adjusting the water bath temperature at 35°C, 45°C and 55°C. The control solution at the same tested temperature was

employed for reference. Other experimental steps are identical as described for the effect of concentration.

3 Results and discussion

3.1 Characteristics of human hair adsorbents

Figure 1 displays the thermal profile of human hair. The initial weight loss of 7% from 33°C to 130°C is due to the release of the physically adsorbed water. The sharp peaks at 249°C and 345°C with 50% weight loss could be attributed to the denaturation of keratin polypeptide chains that make up the morphologies and structures of human hair [21]. Denaturation is a process whereby the proteins lose their original structure, become more simplified, and start to degrade with increasing temperature. The degradation of carbonic chains takes place at a temperature range of 345°C–470°C [22], while a complete degradation of keratin and hair structures was observed at 700°C with residual of 20%.

Table 1 shows the characteristics of human hair adsorbents. The adsorbents exhibit similar yield of $92 \pm 1\%$

Figure 1: Thermogravimetric curve of human hair.

Table 1: Characteristics of human hair adsorbents.

Sample	Yield (%)	pH	Surface area (m ² /g)	EDS (wt%)		
				Carbon	Oxygen	Sulfur
UH	93.0	5.43	1.36	72.3	26.5	1.2
AH	92.0	4.95	1.96	71.6	26.2	2.0
BH	91.2	5.44	3.51	67.5	31.0	1.4

with pH varying between 4.95 and 5.44. The basic-treated human hair adsorbent (BH) displays a higher specific surface area of $3.51 \text{ m}^2/\text{g}$ upon treatment with KOH, while a small increase was observed for HNO_3 -treated one (AH). It is suggested that the basic treatment could be effective to flush the impurities (probably trace oils) on the hair surface, thus exposing the hair structures and also the functional groups. This could be supported by a slight decrease in yield, and an increase in oxygen content (EDS data) for BH.

The infrared penetrates the outer surface of hair, known as cuticle that is primarily composed of cystine, and other amino acids which are not usually found in alpha helical polypeptides [21]. Cystine is an oxidized dimer of amino acid. It contains a disulfide bond (-S-S-) that binds two cystine molecules together, carboxyl group (-CO-OH), and amino group (-NH_2).

From the Fourier transform infrared analysis, all adsorbents exhibit similar spectra signifying the presence of identical surface functional groups. The broad and medium intensity band ranging from 3600 to 3000 cm^{-1} corresponds to the stretches of carboxylic acid (-CO-OH), phenolic (-OH), and amino acid (-NH_2) groups. The peaks located at 1640 cm^{-1} (Amide I), 1520 cm^{-1} (Amide II), 1240 cm^{-1} (Amide III), and 900 cm^{-1} (Amide V) are the characteristics of amino acids, while peaks at 1040 cm^{-1} , 1080 cm^{-1} , and 1120 cm^{-1} are associated with distinct sulfur groups of cystine. The presence of these functional groups is in agreement with the typical chemical constituents of human hair. The variation in peak intensity between the treated human hair-based adsorbents and the untreated one (UH) was not observed.

3.2 Adsorption equilibrium

Figure 2 shows the effect of initial concentration of MB dye on the adsorption performance of human hair as adsorbents. Generally, the adsorption capacity increased with increasing concentration. All adsorbents exhibit a concentration-dependent adsorption due to concentration gradient that provides the driving force to suppress the adsorbent mass transfer resistance for adsorption to take place. To a point of surface saturation, the active sites can no longer accommodate the dye molecules, and consequently the removal capacity begins to level off. The adsorption capacity was found to be in the order of $\text{BH} > \text{UH} > \text{AH}$. This could be explained by the characteristics of BH as displayed in Table 1. BH shows a maximum removal efficiency of 80% ($q_e = 10 \text{ mg/g}$) at $C_o = 13 \text{ mg/l}$, while a higher capacity of 14 mg/g was

Figure 2: Effect of concentration on methylene blue removal by human hair adsorbents (bars: adsorption capacity; lines: removal efficiency).

obtained at $C_o = 42 \text{ mg/l}$ with a decreased efficiency of 33%. The decrease in the removal efficiency is linked with the increase in residual concentration upon equilibrium due to the decrease of vacant sites with increasing concentration. Similar pattern was also demonstrated by AH and UH, with maximum removal efficiency of 22% ($q_e = 3.6 \text{ mg/g}$, $C_o = 17 \text{ mg/l}$) and 30% ($q_e = 3.8 \text{ mg/g}$, $C_o = 13 \text{ mg/l}$), respectively.

Figure 3 shows the equilibrium curves of MB adsorption onto human hair adsorbents. The concave downward pattern indicates a favorable MB adsorption onto human

Figure 3: Equilibrium adsorption of methylene blue onto human hair adsorbents (lines were predicted by, solid: S-shaped isotherm; dashed: Langmuir isotherm).

hair adsorbents. The maximum adsorption capacity of BH was recorded as 13.5 mg/g, while AH and UH shared a similar capacity of 3.4 mg/g. BH exhibits a comparable removal performance with orange peel (surface area = 1.17 m²/g, Q_m = 18.3 mg/g) [16] and *Prosopis sicigera* L. wood (surface area = 121 m²/g, Q_m = 25.1 mg/g) [17].

The adsorption data were fitted into two models, namely Langmuir [Eq. (1)] [23] and S-shaped isotherm [(Eq. (2)), as follows,

$$q_e = \frac{Q_m b C_e}{1 + b C_e} \quad (1)$$

$$q_e = \frac{Q_m}{1 + e^{-b(C_e - m_e)}}, \quad (2)$$

where Q_m (mg/g) is the maximum adsorption capacity, b (l/mg) is the adsorption affinity, and m_e (mg/l) is the midpoint equilibrium concentration. The isotherm constants were solved by nonlinear regression using *Solver-add* in MS Excel for the least sum-of-squared error (SSE) that yields the optimum coefficient of determination, R^2 . Table 2 summarizes the values of isotherm constants. The adsorption data fitted well into S-shaped isotherm. This is true for all adsorbents studied. It implies that the adsorption did not follow an ordinary Langmuir isotherm that describes a monolayer adsorption onto homogeneous adsorbent surface [23]. Rather, the S-shaped isotherm suggests a cooperative adsorption, whereby the already adsorbed dye molecules formed a layer to attract the mobile molecules in the bulk solution to be captured as well [24]. It is evident from Figure 3, where the uptake capacity is initially small at low equilibrium concentration to a point where the capacity displays a sudden steep increase with a small increase in concentration which renders a maximum value of adsorption capacity.

The S-shaped isotherm satisfactorily predicts the maximum adsorption capacity from the experimental data (Table 2). Despite having an identical maximum capacity, AH reaches the same point at a higher equilibrium concentration compared to UH. It could be due to the protonated surface of AH (pH = 5.0, pH_e = 5.2) that somewhat

hinders and drives away the positively charged MB molecules at lower concentration, leading to a lower removal efficiency. However, this was somewhat overcome as the concentration increases because of the increase in the interaction probabilities.

The adsorption of MB onto human hair could be driven by surface functional groups. During KOH treatment, oil covering the hair surface is removed, thus exposing the surface functional groups and thereby increasing the specific surface area. The main component in hair is cystine, while the probable functional groups for adsorption are amine ($-NH_2$), phenolic ($-OH$), and lactonic ($=O$). Amine has one lone pair electron, while phenolic and lactonic possess two lone pair electrons. Hence, they are all electron donating groups that are prone to release electron to the oxidizing agent or electron withdrawer/acceptor (MB). However, based on the electronegativity rule, oxygen is more electronegative than nitrogen that implies a stronger hold of electrons by oxygen. Hence, it is presumed that the adsorption of methylene is much easier on the amine groups compared to the oxygen groups. The following mechanisms can be proposed for MB adsorption onto human hair.

Figure 4 shows the effect of solution pH on MB adsorption onto basic-treated human hair adsorbent (BH). For the two concentrations studied, a similar pattern of pH-dependent adsorption was demonstrated, in which the adsorption of MB increased with increasing solution pH. The trend is more pronounced for C_0 = 10 mg/l. This could be attributed to the isoelectric point (pI) of human hair which is in the range of 2.45–3.17 [25]. The solution pH affects the adsorbent surface charge through the dissociation of functional groups, and the degree of ionization of dye molecule. The surface charge of human hair is positive when the solution pH is below pI due to the protonated surface by hydrogen ions, while the surface becomes negatively charged when the solution pH is

Table 2: Constants of isotherm models.

Adsorbent	Equilibrium pH, pH_e	Langmuir				S-shaped				
		Q_m (mg/g)	b (l/mg)	SSE	R^2	Q_m (mg/g)	b (l/mg)	m_e (mg/l)	SSE	R^2
UH	5.4 ± 0.1	14.3	0.0203	4.69	0.726	3.36	1.02	6.83	1.67	0.896
AH	5.2 ± 0.2	5.16	0.0457	7.66	0.496	3.35	7.31	12.1	1.16	0.948
BH	6.0 ± 0.1	17.4	0.259	51.7	0.734	13.5	1.45	2.58	21.3	0.883

Figure 4: Effect of solution pH on the removal of methylene blue by basic-treated human hair adsorbent.

greater than pI. As a result, the electrostatic interaction/attraction between the deprotonated surface and the positively charged MB molecules increased with increasing solution pH [26]. However, extra caution should be taken as the increase of solution pH could in some way affect the wavelength and density of the solution, thus nullifying the concentration value (e.g., for pH 10, before pH adjustment $C_0 = 10$ mg/l, after pH adjustment $C_0 = 18$ mg/l).

3.3 Rate of adsorption

Figure 5 displays the rate of MB adsorption by BH at three selected concentrations, i.e. 5, 13, and 25 mg/l. A rapid adsorption was observed in the first 2.5 h, after which the removal capacity starts to level-off at different values depending on the concentrations used. The initial fast removal is due to high concentration gradient and unoccupied active sites on the adsorbent surface. As the MB molecules start to lodge on the active sites, the remaining molecules in the bulk solution become lesser thus decreasing the rate of adsorption ($dC_t/dt \rightarrow 0$).

The quasi-equilibrium was observed at around 6 h, with $q_t = 13.5$, 8, and 3.5 mg/g with descending concentrations. Later at $t > 17$ h, a jump in MB adsorption was detected for concentrations 13 and 25 mg/l, thus creating an additional adsorption isotherm. The q_e values obtained after 17 h are in agreement with the data shown in Figures 2 and 3. From Figure 5, it can be generalized that the actual equilibrium for higher concentrations could be attained at $t > 17$ h, while a shorter period may be sufficient for lower concentrations. This also supports the hypothesis

Figure 5: Rate of methylene blue adsorption by basic-treated human hair adsorbent (Lines were predicted by pseudo-first-order and S-shaped kinetics models).

of cooperative adsorption as described by the S-shaped isotherm earlier.

The kinetics data were evaluated using the pseudo-first-order [Eq. (5)] [27], pseudo-second-order [Eq. (6)] [28], and intraparticle diffusion [Eq. (7)] [29] models for the rate-controlling steps. The kinetics models are given as follows,

$$q_t = q_e (1 - e^{-k_1 t}) \quad (5)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (6)$$

$$q_t = K_p t^{0.5} + C. \quad (7)$$

where q_t (mg/g) is the amount of MB adsorbed at time t (h), k_1 (h^{-1}), k_2 ($\text{g}/\text{mg} \cdot \text{h}$), and K_p ($\text{mg}/\text{g} \cdot \text{h}^{0.5}$) are the rate constants for the pseudo-first-order, pseudo-second-order and intraparticle diffusion models, respectively, and C (mg/g) is the intercept that gives an idea about the boundary layer thickness. A generic model, namely S-shaped kinetics [Eq. (8)] was also introduced to represent an increase in the adsorption capacity at $t > 17$ h for $C_0 = 13$ and 25 mg/l. It is expressed as,

$$q_t = \frac{q_e}{1 + e^{-k_s(t-m_t)}}, \quad (8)$$

where q_e (mg/g) is the equilibrium capacity, k_s (h^{-1}) is the rate constant, and m_t (h) is the midpoint of time. All kinetics constants were solved using *Solver* add-in of Microsoft (MS) Excel, and the values are summarized in Table 3.

Table 3: Constants of kinetics models.

	5 mg/l	13 mg/l	25 mg/l
Pseudo-first-order^a			
q_e (mg/g)	3.52	8.01	13.1
k_1 (h ⁻¹)	0.307	1.27	0.931
R^2	0.983	0.991	0.987
SSE	0.570	1.48	6.01
Pseudo-second-order^a			
q_e (mg/g)	3.95	8.85	15.2
k_2 (g/mg · h)	0.101	0.203	0.0749
R^2	0.972	0.972	0.986
SSE	0.919	4.21	5.92
S-shaped kinetics^b			
q_e (mg/g)	–	9.97	17.8
k_s (h ⁻¹)	–	0.157	0.157
m_t (h)	–	8.14	9.38
R^2	–	0.895	0.979
SSE	–	0.516	0.532

^aConstants predicted for $0 < t < 17$ h. ^bConstants predicted for $t > 17$ h.

From Table 3, the kinetics data for $t < 17$ h were well fitted into the pseudo-first-order model with reasonably high R^2 , and a good approximation of q_e (or quasi q_e for $C_0 = 13$ and 25 mg/l) to the experimental data. The applicability of this model for the stated adsorption period indicates that the external diffusion is a significant step [4]. Also, the rate constant, k_1 increased with increasing concentration, signifying a faster adsorption at a higher concentration, and therefore the favorability of adsorption as the concentration increases. This could be seen from the change in the gradients of q_t vs. t as shown in Figure 5. Depending on the availability of active sites, the adsorbent can accommodate a higher adsorbate concentration for a higher removal capacity. However, the adsorption rate is likely to slow down due to the inherent repulsion between the neighboring adsorbate molecules, and the competition for the active sites. Because of that, k_1 may as well decline at higher concentration (for $C_0 = 25$ mg/l).

For the whole adsorption period, the pseudo-first-order model could only satisfy the adsorption data of $C_0 = 5$ mg/l. Hence, a generic S-shaped kinetics model was used to describe a sudden increase in the adsorption after quasi-equilibrium at $t > 17$ h for $C_0 = 13$ and 25 mg/l. From Table 3, this model satisfactorily fitted the remaining data with a good prediction of q_e as that of the experimental data (Figure 5). In addition, the values of rate constant, k_s for both concentrations are comparable, but somewhat lower compared to that of k_1 . It indicates that the cooperative adsorption onto the already adsorbed dye molecules occurs at a same rate, which is much slower than the initial

Figure 6: Intraparticle diffusion plots.

adsorption by the role of surface functional groups. The possible mechanism for the cooperative adsorption is π - π interaction among the aromatic rings of MB molecules. The aromatic (benzene) ring enables the π -electrons to delocalize, thus prompting a weak attractive force towards its neighboring molecule [30]. The contact may become more effective because the already adsorbed dye molecules had lost their cationic character as a result of anchoring onto the surface functional groups at quasi-equilibrium.

Figure 6 displays the intraparticle diffusion plots. In general, all lines are not linear through origin, where each line can be split into two or three connecting lines of different slopes. Because of that, the intraparticle diffusion is not the only rate-limiting step that controls the adsorption [5]. From Figure 6, the first part of the line indicates the initial stage of adsorption, and reflects the thickness of boundary layer, while the second and the third parts represent the effect of intraparticle diffusion (adsorption) and cooperative adsorption, respectively. Hence, the rate-limiting step (slowest step) could be film diffusion to overcome the adsorbent mass transfer resistant. The time taken to attain the quasi-equilibrium ($t < 17$ h), in general, also infers that the adsorption process is possibly film diffusion-controlled [31]. Therefore, the adsorption of MB onto basic-treated human hair could be based on the following mechanisms: (i) film/external diffusion (slowest step), (ii) intraparticle diffusion (adsorption), and (iii) cooperative adsorption.

3.4 Adsorption thermodynamics

Figure 7 shows the removal of MB dye onto basic-treated adsorbent at different temperatures. Generally, the

Figure 7: Effect of temperature on methylene blue removal by basic-treated human hair adsorbent.

adsorption slightly increased with increasing temperature, indicating that the process is temperature-dependent and endothermic. The thermodynamics properties, i.e. enthalpy of adsorption (ΔH), Gibbs energy (ΔG), and entropy (ΔS) were calculated using the Gibbs expression as follows,

$$\ln K = \frac{-\Delta G}{RT} = \frac{-(\Delta H - T\Delta S)}{RT} \quad (9)$$

where, $K = C_{e,a}/C_e$ is the equilibrium constant, $C_{e,a}$ (mg/l) is the amount of dye adsorbed, T (K) is the absolute temperature of solution, and $R = 8.314$ J/mol · K is the gas constant. The respective thermodynamics data are summarized in Table 4.

From Table 4, the adsorption of MB onto BH is exothermic at lower concentration, and becomes more endothermic as the concentration increases. The higher the

concentration the greater the energy is absorbed during the adsorption. This is in accordance with the adsorption behavior that increased with increasing temperature. Likewise, the adsorption system demonstrates an increasing disorder or randomness because of the accumulation of dye molecules on the surface as the concentration increases. It is shown by the positive ΔS ($\Delta S = 18.1$ J/mol · K, $C_0 = 20$ mg/l), which also signifies that the process (or system) is feasible [32]. In general, the negative values of ΔG indicate that the MB adsorption onto BH is spontaneous. However, the spontaneity of the process decreased with increasing concentration. For example, the ΔG increased from -3.1×10^{-3} to -4.6×10^{-2} J/mol with increasing concentration from 5 to 20 mg/l at 35°C. This could be partly due to the nature of cooperative adsorption, whereby a concentration gradient is required as the driving force for subsequent increase in capacity after reaching the quasi-equilibrium. Nevertheless, the spontaneity of the process slightly improved as temperature increases to 55°C at $C_0 = 20$ mg/l (ΔG decreased from -4.6×10^{-2} to -8.2×10^{-2} J/mol), signifying the positive effect of temperature as the driving force for adsorption at higher concentration [32, 33].

4 Conclusion

Human hair was used as an adsorbent for MB dye removal from water. All adsorbents, i.e. the untreated, HNO_3 -treated and KOH-treated human hair samples exhibit an S-shaped isotherm, suggesting a cooperative adsorption. The basic-treated human hair (BH) displays a superior removal of MB compared to other two counterparts. The removal of residual oil covering the human hair surface by KOH, possibly exposes the functional groups thus increasing the effective surface area and the removal performance. The maximum capacity of BH was recorded as 13.5 mg/g. Further evaluation on the effect of time revealed a sudden increase in the adsorption capacity after a 17 h quasi-equilibrium for MB concentrations of 13 and 25 mg/l. The mechanisms of adsorption could be summarized as: (i) external diffusion, (ii) adsorption, and (iii) cooperative adsorption. The adsorption process is endothermic and spontaneous with increasing temperature especially at high MB concentration.

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Table 4: Thermodynamics properties of methylene blue adsorption by basic-treated human hair adsorbent.

C_0 (mg/l)	T (K)	ΔG (J/mol)	ΔH (J/mol)	ΔS (J/mol · K)
5	308	-3.09×10^3	-4153	-3.46
	318	-3.05×10^3		
	328	-3.02×10^3		
10	308	-2.18×10^3	-611	5.10
	318	-2.24×10^3		
	328	-2.29×10^3		
20	308	-4.59×10^2	5116	18.1
	318	-6.58×10^2		
	328	-8.21×10^2		

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