Sorption Mechanism and Performance of Peat Soil Humin for Methylene Blue and *p*-Nitrophenol

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Abstract: *The responsible mechanism and performance of peat soil humin for the sorption of methylene blue (MB) and* p*-nitrophenol (*p*-NP) have been investigated. Humin was obtained from peat soil of Siantan, West Kalimantan, Indonesia, after removing the content of humic and fulvic acids into a NaOH solution using the recommended procedure of International Humic Substances Society (IHSS). The obtained humin was then purified by rigorous stirring in a mixed solution of HCl 0.1 M and HF 0.3 M. Ash content in humin after the purification abruptly decreased from 36.84 to 1.26 wt.% indicating that minerals and other inorganic impurities were mostly removed. Phenolic –OH and carboxyl (–COOH) functional groups contributing to the acidity of humin were in the level of 3.44 and 2.10 mmol/g, respectively. At optimum medium pH of 6.20 for MB and 7.00 for p-NP, $-COO^-$ as the deprotonated product of –COOH was the most responsible active site in sorbing MB and* p*-NP through electrostatic interaction and hydrogen bonding, respectively. The homogeneity of $-COO^-$ as the active site for the sorption of MB and p-NP implied that the surface of humin sorbent was energetically uniform and thereby the sorption of both MB and p-NP followed better the Langmuir than the Freundlich isotherm model with sorption capacity of 0.19 and 0.26 mmol/g and sorption energy of 32.92 and 27.27 kJ/mol, respectively.*

Keywords: *sorption; mechanism; humin; peat soil; methylene blue;* p-nitrophenol

■ INTRODUCTION

Synthetic dyes are very common in our daily life and their demand continuously increases because of the growth of human population and rapid development of industries. It is forecasted that the total dye market increases at an average annual rate of about 3% [1]. Although synthetic dyes are used in various areas such as textile, paper, printing, plastic, cosmetic, wood, food, etc. [2], textile industries are still the primary consumer. As for 2014, the textile industries contribute for more than half of the world dye and organic pigment demand [1]. Since the efficiency of using dyes in the common industries is in the range of 60 to 80%, so 20 to 40% of dyes used in industries will be discharged to the environment [3]. The discharge of dyes in the environment is a matter of attention for both toxicological points of view and esthetical reason.

Among the commonly discharged dyes, methylene blue (MB) and *p*-nitrophenol (*p*-NP) received a primary concern because of their harmful effects to many forms of life. Methylene blue can cause harmful effect to an organism such as mild bladder irritation, dizziness, headache, increased sweating, nausea, and diarrhea [4]. *p*-nitrophenol causes headaches, drowsiness, nausea, and cyanosis if ingested [5]. The harmful effects, such as the death of aquatic life, inhibition of the normal activities of microbial community and carcinogenicity to animals, have been proved by increasing evidence [6]. Given these adverse effects coupled with the wide prevalence and poor biodegradability of MB [7] and *p*-NP [8], it is necessary to understand the fate and behavior of MB and *p*-NP in the environment.

With the presence of recent trend of geographical shifts of the location of textile industries from China to

South East Asian countries such as Vietnam and Indonesia which have large peat soil area [9], the understanding of the fate and dynamics of MB and *p*-NP in peat soil is increasingly important. Indeed, Indonesia occupies a position as the country with the highest tropical peat soil area in the world [10].

As a type of organic soils, peat soil contains mainly humic substances. Compared to the two other fractions of humic substances, i.e. fulvic and humic acids, humin is the biggest fraction [11]. Accordingly, the ability of humin to interact with MB and *p*-NP and the responsible mechanism controlling that interaction become important aspects to be necessarily examined to gain an understanding of the fate and dynamic of MB and *p*-NP in peat soil. The effects of solution pH and initial concentrations of MB and *p*-NP have been studied to achieve the aforementioned aims and eventually the adsorption mechanism of MB and *p*-NP on humin from peat soil was elucidated.

■ EXPERIMENTAL SECTION

Materials

All reagents in analytical grade, i.e., MB (basic blue 9, molecular weight 373.91 g/mol), *p*-NP (molecular weight 139.1 g/mol), NaOH, BaOH, HCl, HF, H_2SO_4, ethanol, calcium acetate, and dimethyl sulfate, were purchased from Merck Co Inc. (Germany) and used without further purification. The sorption studies for MB and *p*-NP were carried out with fresh solutions that were prepared from a 1000 mg/L stock solution. Peat soil as a source of humin was taken from Siantan Hulu, West Kalimantan, Indonesia.

Instrumentation

X-ray diffractometry (XRD) (Mac Science MXP3), Fourier-transform infrared spectroscopy (FT-IR) (Shimadzu Prestige-21) and scanning electron microscopy (SEM) (SEMEDAX JSM 6360 LA) were used to characterize humin. A Hitachi 150-20 UV-Vis spectrometer operating in the absorbance mode was employed for the determination of MB and *p*-NP in the sample solution. The determination was conducted at λ_{max} which varied depending on the pH of the sorption medium. The measurement of pH of sample solutions was carried out by using a Metller Toledo pH meter.

Procedure

Preparation of humin sorbent

Humin sorbent was obtained from peat soil after removing the fractions of humic and fulvic acids as well as purifying the obtained crude humin to pure humin from any mineral impurity by using a mixed solution of HCl 0.1 M and HF 0.3 M. The removal of humic and fulvic acids from the peat soil sample to obtain crude humin was performed according to the recommended procedure of International Humic Substances Society (IHSS) which was modified by Santosa et al. [11].

Peat soil was first dried under a nitrogen atmosphere in a container having no direct contact with sun light and then ground and sieved to pass through 200-mesh of sieving apparatus. The dry peat soil powder was shaken for 24 h in NaOH 0.1 M under a nitrogen atmosphere with the weight of peat soil powder (g) and the volume of NaOH solution (mL) ratio was 1:10. The mixture was centrifuged at a rate of 2000 rpm for 10 min to settle down suspended material and followed by filtration with 0.45 µm cellulose nitrate filters to separate the suspended material from the supernatant. The suspended material was dried in an oven at the temperature of 50 °C and then ground and sieved to pass through 200-mesh of sieving apparatus to obtain crude humin powder. The crude humin was purified by immersing in a mixed solution of HCl 0.1 M and HF 0.3 M and shaking at room temperature for as long as 24 h. The mixture was centrifuged to separate suspended material from supernatant at a rate of 2000 rpm for 10 min. This purification procedure was repeated until the ash content was lower than 2 wt.%. Before drying in an oven at a temperature of 50 °C and then grinding and sieving to pass through 200-mesh of sieving apparatus to obtain purified humin powder, the purified suspended material was intensively rinsed with water to give a neutral supernatant. The ash content was determined by drying the humins in an oven at a temperature of 600 °C to obtain a constant weight. The ash content was the ratio of the remaining weight after heating to the initial weight of the material.

The crude and purified humins were qualitatively characterized using FT-IR spectroscopy and XRD. In addition to qualitative characterization, the crude and purified humins were quantitatively determined for their total acidity and their carboxyl (–COOH) functional group content. Total acidity and –COOH group were determined by barium hydroxide and calcium acetate methods, respectively [12]. From these total acidity and –COOH group content, phenolic –OH group content was then calculated by subtracting the –COOH content from the total acidity.

Sorption of MB and p*-NP*

Sorption of MB and *p*-NP from its aqueous solution using the purified humin as sorbent was performed by examining the effects of medium acidity and initial concentration of MB and *p*-NP.

Effect of medium acidity. A series of 50 mL of MB 10 mg/L solutions at pH 2.00, 4.00, 6.00, 8.00, 10.00, and 12.00 was first prepared. HCl or NaOH solution was used to adjust the pH of those MB solutions. Into every MB solution, 50 mg of humin sorbent was added and stirred for 2 h in a batch-type reactor at 25 ± 0.1 °C. After separation through 0.45-µm cellulose nitratefilter, the concentration of MB in the supernatant was analyzed spectrometrically by ultraviolet visible (UV-Vis) spectrometer (Hitachi 150-20) at a wavelength of maximum absorbance (λ_{max}) at 665 nm. It has been examined that initial pH (ranging from pH 2.00 to 12.00) of MB solution had no noticeable effect on the λ_{max}, indicating stability of MB within the studied range of pH. The same evidence was observed by Gupta et al. [13].

Every sample was accompanied by a blank solution containing no sorbent, and both of them were treated and analyzed under the same condition. The amount of MB removed from the solution was considered to be the difference between the initial and remaining amount of MB in the reacting solution after contact time 2 h.

In addition to MB, the same experimental procedure was conducted for *p*-NP. However, the quantification of *p*-NP was done at λ_{max} ca. 320 nm instead of 665 nm. The λ_{max} of *p*-NP slightly varied around 320 nm with the change of pH of sorption medium.

Effect of initial concentration. Experiments were conducted using a batch-type reactor at 25 ± 0.1 °C. Into 50 mL of solutions containing various concentrations (2 to 100 mg/L) of MB at pH 6.00, as much as 50 mg of humin sorbent was added and stirred for as long as 2 h. After separating supernatants, concentrations of MB in the supernatants were determined spectrometrically at λ_{max} 665 nm. Under the same condition as a sample solution, a blank solution was also analyzed. The same experimental procedure was also performed for *p*-NP, but the measurement was done at λ_{max} 320 nm.

RESULTS AND DISCUSSION

Preparation and Characterization of Humin Sorbent

Crude humin obtained after the removal of humic and fulvic acids from the alkaline extraction of peat soil contained more than 20 wt.% of mineral impurities (ash) (Table 1). To remove ash content in humin, we previously employed a mixed solution of HCl 0.1 M and HF 0.05 M [11]. Unfortunately, with this proportion of mixed solution, we were only able to reduce the ash content from 30.7 to 22.0 wt.% after three times consecutive purification. Considering that the ash content in humin mostly consisted of SiO_2 [11], we employed a mixed solution of HCl and HF with higher proportion of HF, i.e. HCl 0.1 M and HF 0.3 M. By employing this new composition of a mixed solution, the ash content of humin sharply decreased from 20.01 to 1.26 wt.% after three times consecutive purification (Table 1).

Previous evidence that SiO_2 was the main impurity of the humin's ash component was confirmed in Fig. 1. XRD spectra of the crude and purified humins in Fig. 1 showed that SiO_2 in the form of quartz mineral, whose

Table 1. Functional group determination and ash content of crude and purified peat soil-derived humins

Humin	Parameters determined		
	Functional group (mmol/kg)		Ash content (wt%)
	Carboxyl	Phenolic-OH	
Crude	371	3398	20.01
Purified	2100	3435	1.26

presence was indicated by a sharp peak at a 2θ value of 26.27°, was the only noticeable inorganic impurity in the humins. The intensity of SiO_2 peak in the spectrum of the purified humin appeared much smaller than that in the corresponding spectrum of the crude humin, thereby supporting the ash content data listed in Table 1 which indicated that the purified humin contained less ash than the crude humin. A very similar result was observed for Brazilian tropical peat soil. In that case, after treatment with HCl 1.0 M, the amorphous pattern of the peat soil was modified by the appearance of a sharp peak at a 2θ value of ca. 26°, which is typical for a quartz peak [14].

Purification using the mixed solution of HCl 0.1 M and HF 0.3 M abruptly improved the concentration of –COOH groups, but the concentration of phenolic –OH groups remained relatively constant at ca. 3400 mmol/kg. Before purification, the concentration of –COOH group was 371 mmol/kg, and it greatly increased to 2100 mmol/kg after purification (Table 1).

A significant increase on the concentration of –COOH group after purification was supported by the results of characterization using FT-IR spectroscopy. Purification caused the appearance of a new absorption band at 1705 cm^{-1} but suppression of the absorption bands at 1377 and 1087cm^{-1} (Fig. 2). As has been very frequently observed for humic substances, particularly for humic acid [15-16] and humin [11,17], their interaction with metal cations lead to the suppression of that absorption band at ca. 1705 cm^{-1} and appearance of a new band at 1377 cm^{-1}. The absorption band at 1705 cm^{-1} corresponds to the stretching vibrations of C=O in –COOH functional groups, while the absorption band at 1380 cm^{-1} is interpreted to result from the interaction between –COOH group and a metal cation through a cation exchange. Thereby, the appearance of new absorption bands at 1705 cm^{-1} and suppression of the absorption band at 1377 cm^{-1} after purification of the crude humin, may reasonably be interpreted as due to the release of significant numbers of –COOH groups from their interaction and association with their various impurities. This interpretation is in accordance with the quantitative data for the concentrations of –COOH and phenolic –OH functional groups in Table 1. According to the data in Table 1, purification was able to enhance the concentration of –COOH group by approximately 5.7-fold, while that of the phenolic –OH group remained relatively constant.

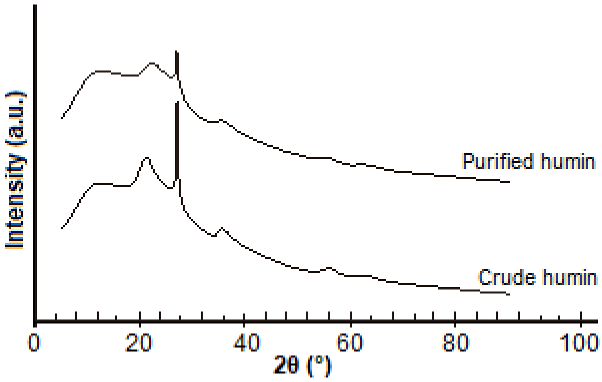

Fig 1. Powder XRD pattern of crude and purified humins derived from peat soil

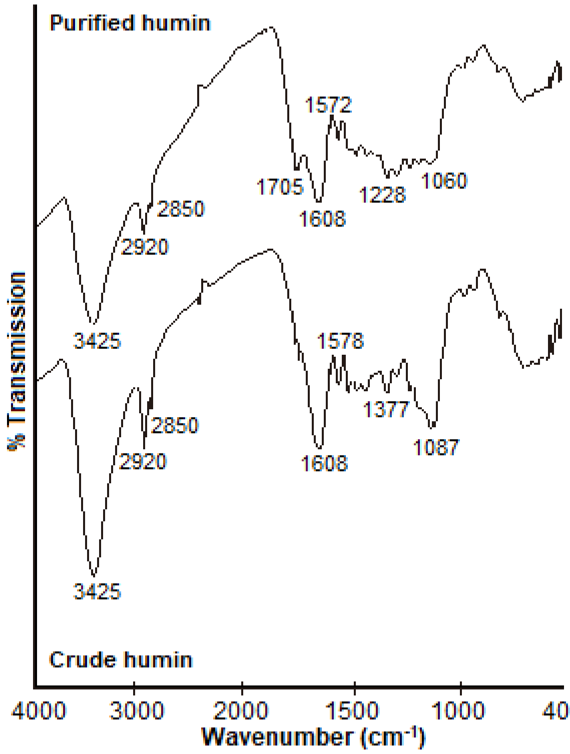

Fig 2. FT-IR spectra of crude and purified humins derived from peat soil

The suppression of absorption bands at ca. 1087 cm^{-1} after purification may be interpreted as the result of the removal of inorganic components such as SiO_2. As observed previously, SiO_2 and Al_2O_3 were the main impurities of crude humin and their absorption

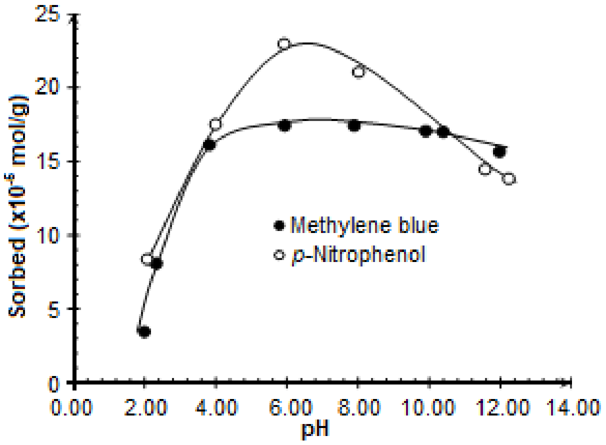

Fig 3. Sorption profiles of methylene blue (MB) and *p*-nitrophenol (*p*-NP) on humin as a function of equilibrium pH

bands were suppressed after purification using mixed solution consisting of HCl and HF [11].

Sorption of Methylene Blue and *p*-Nitrophenol

Effect of medium acidity

The acidity of sorption medium is an important factor for sorption process because it affects the ionization of dye molecule and charge intensity of sorbent surface. As indicated in Fig. 3, the increase in the solution pH from 2.00 to 6.00 was helpful for the sorption of MB and *p*-NP onto humin sorbent. As initial solution pH increased from 2.00 to 6.20, the sorbed MB rapidly increased from 3.45 to 17.42 x 10^{-5} mol/g. The similar evidence was observed for *p*-NP, i.e. the sorbed *p*-NP enhanced from 8.36 to 22.95 x 10^{-5} mol/g as the solution pH moved from 2.10 to 6.10.

As indicated in Table 1, humin is rich in –OH and –COOH functional groups and these groups, especially the –COOH group, has been known for a long time as the most reactive in attracting metal cations [18-19]. This finding has also been confirmed by more recent studies [16,20]. The amount of un-ionized –COOH functional groups in humic substances decreases with the increasing of medium pH. This decrease is slow over the range 2.00 < pH < 4.00, changes to a very rapid increase from pH 4.00 to 5.00, and changes again to a slow increase at pH values above 5.00. At pH 6.00, nearly all of the –COOH groups have been ionized [15,21].

Methylene blue with pKa > 14 [22], is positively charged on the entire studied pH range and it will be attracted well onto sorbent's negatively charged sites because of electrostatic attraction. As solution pH increased, the number of negatively charged surface sites on the adsorbent enhanced, which may result in the increase of adsorption of this positively charged MB. Therefore, the rapid increase on the sorption of MB from pH 2.00 to 6.20 may be interpreted as the result of the more intense attraction of positively charged MB on humin sorbent which is more negatively charged at higher pHs.

After reaching maximum at pH 6.20, sorption of MB started slightly decreasing with increasing pH. Although the negatively charged surface sites on the sorbent increase with increasing pH, but the proportion of OH^- in the solution also increases and becomes more dominant than H^+ at medium pH higher than 7.00. This increasing of OH^- will be a serious competitor to the negatively charged surface sites on the sorbent in interacting with the positively charged MB. Therefore, instead of increasing, the sorption of MB on humin sorbent slightly decreased with increasing of medium pH from 6.2.

In contrast to MB, *p*-NP may exist in neutral or negatively charged species depends on the medium pH. Since *p*-NP possesses pKa value 7.15 [6], it will be more dominant in the form of a neutral molecule at pH lower than 7.15 and changes to an anion as the more dominant species at medium pH higher than 7.15. This change from neutral to negatively charged species over the studied medium pH yielded more variation on the amount of *p*-NP sorbed on humin sorbent if compared to the sorption of MB (Fig. 3). Indeed after the sorption of *p*-NP increased abruptly from medium pH 2.10 to approximately 7.0, the sorption sharply decreased in alkaline medium. As described before, the negatively charged surface sites on the humin sorbent enhance with increasing medium pH. However, this negative charge enhancement will only give significant positive effect on the sorption of *p*-NP in the medium pH lower than the pKa value of *p*-NP when the *p*-NP is dominantly present in neutral species. When the medium pH exceeds the pKa value of *p*-NP, the positive effect changes to adverse effect since *p*-NP will force with the negatively charged active sites of humin sorbent.

Effect of initial concentration

The experimental data on the sorption of MB and *p*-NP on humin sorbent at temperature 25 ± 0.1 °C as a function of sorbate concentrations at equilibrium are given in Fig. 4. The sorption of both sorbates was non-linear, rapidly increased at a low level of concentration of sorbates and changed to approximately constant when the equilibrium concentration of MB was higher than 5 x 10^{-5} mol/L and moved to small increase when the equilibrium concentration of *p*-NP was above 15 x 10^{-5} mol/L.

Two widely used isotherm models, i.e. Langmuir and Freundlich were applied for the fitting of the experimental data. The Langmuir model is mathematically represented in Eq. (1)

$$m = \frac{bKC}{1+KC} \quad \text{or} \quad \frac{C}{m} = \frac{1}{bK} + \frac{C}{b} \qquad (1)$$

where C is the equilibrium concentration of remaining sorbate in solution, b is the Langmuir sorption capacity, K is the sorption affinity, and m is the amount of sorbate per unit mass of sorbent at equilibrium. K is a constant that is related to the heat of sorption. If the sorption follows the Langmuir model, b and K can be obtained from the slope and intercept of the plot of C/m versus C.

The Freundlich isotherm model is mathematically represented in Eq. (2).

$$m = BC^{1/n} \ \text{or} \ \log m = \log B + \frac{1}{n} \log C \qquad (2)$$

where B represents the Freundlich sorption capacity and n is a constant. B also represents the average affinity of sorbate toward the active site of sorbent. 1/n represents the degree of dependence of sorption on equilibrium concentration and it is an indicator of sorption intensity [23]. If the sorption fulfills the Freundlich model, B and the constant of 1/n can be determined from the intercept and slope of the plot of log m against log C, respectively.

Application of Eq. (1) and (2) to the sorption data in Fig. 4 yielded sorption parameters as given in Table 2. As indicated by the value of correlation coefficient (R^2), the sorption of both MB and *p*-NP followed better the Langmuir than Freundlich isotherm model. The more applicability of the Langmuir than the Freundlich isotherm model in describing the adsorption data in Fig. 4 indicates that the surface of humin sorbent is energetically uniform [24]. It means that in spite of the humin sorbent contained phenolic –OH and –COOH groups at a relatively comparable concentration (Table 1), but only one of them which much more actively attract MB and *p*-NP sorbates. Considering –COOH has been confirmed by numerous studies to possess much higher reactivity than phenolic –OH group towards metal cations [16,18-20], so it is also reasonable to assume that this –COOH group is the most responsible functional group in binding *p*-NP and especially MB which is positively charged like metal cation.

Methylene blue is positively charged on the entire studied pH range [22], while *p*-NP changes from neutral to negatively charged species at medium pH > 7.15 [6]. Since the active sites of humin sorbent shift from mostly neutral at typically pH 2.00 to more negatively charged at higher pHs, so the affinity of the humin sorbent (K) toward MB will be higher than *p*-NP. The data summarized in Table 2 confirmed this suggestion, i.e. the K values of humin toward MB and *p*-NP were 5.89 and 0.60 x 10^5 $(mol/L)^{-1}$, respectively. By using these K values, the calculated sorption energy (E) of MB (32.92 kJ/mol) was bigger than that of *p*-NP (27.27 kJ/mol).

In contrast to sorption energy, the sorption capacity of humin sorbent for *p*-NP (26.32 x 10^{-5} mol/g or

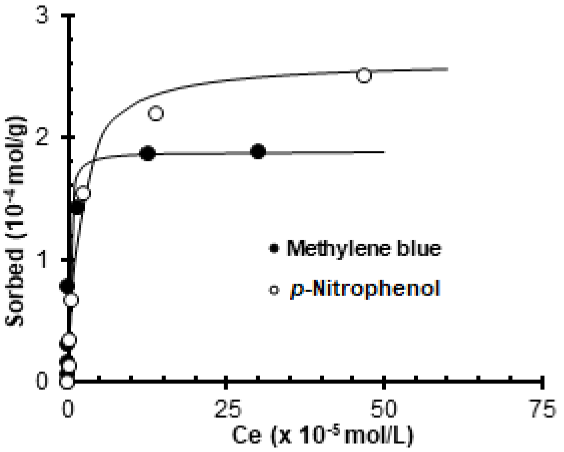

Fig 4. Sorption of methylene blue (MB) and *p*-nitrophenol (*p*-NP) on humin as a function of their equilibrium concentrations

Table 2. Sorption capacity (b), affinity (K) and energy (E) obtained from Langmuir isotherm as well as sorption capacity (B) obtained from Freundlich isotherm for the sorption of methylene blue (MB) and *p*-nitrophenol (*p*-NP) on humin at 25 ± 0.1 °C

	Sorption parameters						
Sorbate	Langmuir				Freundlich		
	b (10^{-5} mol/g)	K (10^5 mol/L)$^{-1}$	E*(kJ/mol)	R^2	B (10^{-3} mol/g)	n	R^2
MB	18.87	5.89	32.92	0.998	4.61	3.01	0.891
p-NP	26.32	0.60	27.27	0.997	13.23	2.14	0.854

*E = RT ln K

Table 3. The comparison of Langmuir's sorption capacities of the purified humin and other low-cost sorbents for methylene blue (MB) and *p*-nitrophenol (*p*-NP)

Sorbent	Sorbate	Sorption capacity (mg/g)	Ref
Humin	MB	70.6	This study
Bagasse fly ash		6.5	[13]
Orange peel		18.6	[25]
Citrus maxima peel		28.6	[26]
Phoenix tree leaf		70.9	[27]
Lufta cylindrica fiber		49.0	[28]
Coconut bunch waste		70.9	[29]
Wood apple shell		95.2	[30]
Lotus leaf		221.7	[31]
Cotton stalk		147.1	[32]
Pumice		15.9	[33]
Potato pell		33.6	[34]
Parthenium hystrophorous weed		23.8	[35]
Mg/Al hydrotalcite		7.9	[36]
Sumac leaf		5.8	[49]
Humin	*p*-NP	36.6	This study
Paper mill sludge		0.3	[37]
Petroleum coke		11.1	[38]
Rice husk		15.3	[38]
Coal fly ash		10.8	[39]
Bagasse fly ash		1.2	[40]
Olive cake		1.6	[41]
Montmorillonites		0.05-0.11	[42]
Bentonites		5.5-15.2	[43]
Zeolites		10.0-12.7	[43]
Brazilian peat		23.4	[46]

equivalent to 36.61 mg/g) was higher than that for MB (18.87×10^{-5} mol/g or equivalent to 70.55 mg/g) (Table 2). This evidence must be caused by the fact that *p*-NP (molar weight of 139.1 g/mol) is smaller in size than MB (molar weight of 319.8 g/mol). Therefore, the active sites of humin sorbent will be able to accommodate more *p*-NP than MB.

Results of a literature survey on the sorption capacity values of low-cost sorbents for MB and *p*-NP was summarized in Table 3. From the listed values in Table 3, it is clear that the humin sorbent used in this study has a satisfactorily sorption capacity toward *p*-NP. Although the sorption capacity of MB was not as excellent as *p*-NP, the performance of humin for MB was still comparable to the highly effective sorbents such as phoenix tree leaf, coconut bunch waste and wood apple shell.

Sorption Mechanism

It has been explained previously that the surface of humin sorbent is energetically homogeneous in binding MB and *p*-NP. Although humin contained more phenolic –OH than –COOH group (Table 1), but many studies consistently showed that the –COOH group was much more reactive than –OH group in binding many types of sorbate. In order to judge whether –COOH group is really the most responsible functional group for the sorption of MB and *p*-NP and to trace further the possible interaction that may occur, a characterization using FT-IR spectroscopy has been conducted for humin sorbent after its use for the sorption of MB and *p*-NP at their optimum medium pHs of 6.20 and 7.00, respectively.

Compared to the spectra of the original humin sorbent (purified humin in Fig. 2) that showed the main absorption bands at 1060, 1608, 1705, 2850, 2920 and 3425 cm^{-1}, the spectra of humin sorbent after its use for the sorption of MB and *p*-NP generated new absorption bands at ca.1455 and 1381 cm^{-1} (Fig. 5). The appearance of a new peak at ca. 1455 cm^{-1} as the C=C stretching vibration of the aromatic ring [45] must be contributed by MB and *p*-NP since they both contain an aromatic ring. In the case of the absorption band at ca. 1381 cm^{-1}, numerous studies observed that this absorption band consistently appeared after the binding of metal ions of Cu(II) [15,21], Cr(III) [16], and AuCl$_4^-$ [11] onto the –COOH group of humic substances. The absorption band at the same wave number also appeared at the spectra of Na-humate purchased from Sigma Chemical, USA [15]. Since in this study the absorption band at 1381 cm^{-1} appears after the use of humin to remove MB and *p*-NP, so the –COOH group of humin should be responsible also in binding MB and *p*-NP. From this evidence, it is supposed that the appearance of the absorption band at ca. 1381 cm^{-1} was not only specific for the result of interaction between –COOH group and metal ions but also as the result of interaction between –COOH group and organic sorbate of MB and *p*-NP. The same evidence was observed recently that the sorption of *p*-NP on the Brazilian tropical peat soil leads to the appearance a new absorption band at 1334 cm^{-1} [46].

In fact, –COOH group possesses a specific absorption band at ca. 1720 cm^{-1} due to its C=O stretching vibration. This C=O stretching vibration moves to wave number of about 1381 cm^{-1} when the –COOH group is ionized to –COO$^-$ and interacts with its counterpart [44]. Therefore, any chemical species that can interact with –COO$^-$ as the ionization product of –COOH group will shift the C=O stretching vibration from its original wave number at 1720 cm^{-1} to a new position of about 1381 cm^{-1}. At the optimum medium pHs for the sorption of MB and *p*-NP, nearly all –COOH groups of humin sorbent are ionized to –COO$^-$ and then interact with MB and *p*-NP to give the aforementioned significant shift of the C=O stretching vibration.

Additionally, the presence of MB on the humin sorbent after sorption was also supported by the increasing

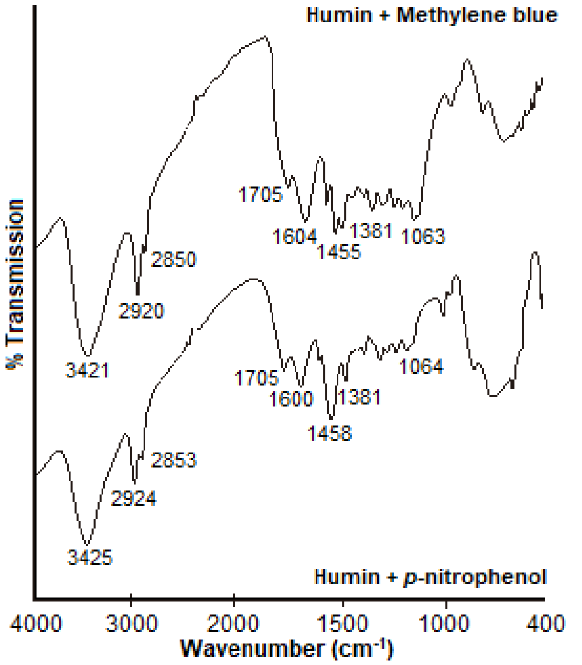

Fig 5. FT-IR spectra of the purified humin sorbent after its use for the sorption of methylene blue (MB) and *p*-nitrophenol (*p*-NP) from aqueous solution

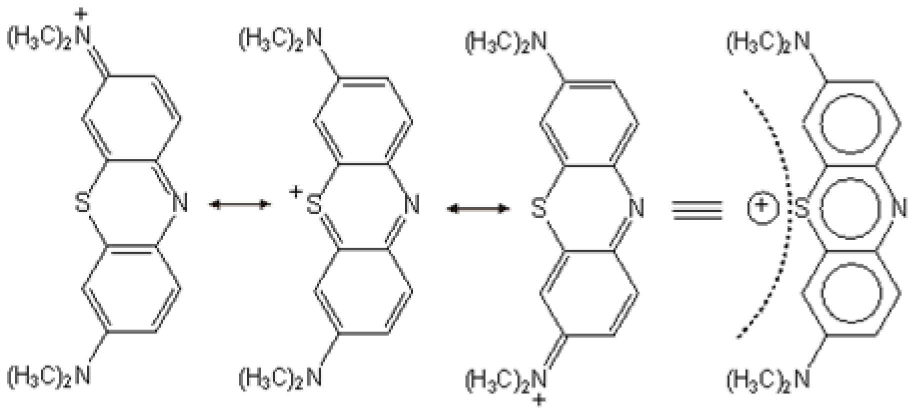

Fig 6. Resonance structures of methylene blue (MB) showing the delocalization of its positive charge

of the intensity of absorption band at 2920 cm^{-1} (Fig. 5). The absorption band at 2920 cm^{-1} is characteristic for the C-H asymmetric stretching of CH_3 or CH_2. Since MB contains CH_3 groups, these CH_3 groups of MB add the number of CH_3 groups in humin and therefore enhance the absorption band at 2920 cm^{-1}.

As positively charged species, the positive charge of MB is not localized on a specific element, but it is delocalized to the entire aromatic rings and nitrogen elements of the MB's side groups (see Fig. 6). Hence, the most reasonable interaction that occurs between humin sorbent and MB sorbate is an electrostatic interaction through negatively charged carboxyl group ($-COO^-$) and the delocalized positive charge of MB (Fig. 7). This proposed mechanism of MB sorption on humin is in some extents similar with the proposed sorption mechanism of MB on an ultrasonically modified chitin [45]. It was claimed that the sorption of positively charged MB on the modified chitin at 298 K was governed by one or two receptor sites (probably hydroxyl and N-acetyl groups) on the modified chitin. Confusing was then observed, however, when the sorption was done at higher temperatures. At temperatures 308, 318 and 328 K, the number of sorbed molecule per receptor site of sorbent (denoted as *n*) became higher than 1, and they then claimed that the every sorbed MB was bound by two receptor sites by a perpendicular anchorage. If it is the case, every MB species needs more than one receptor site and consequently the value of *n* will be smaller than 1 not higher than 1. As MB is a relatively big in size (molar weight of 319.8 g/mol), it is hard to imagine that every receptor site on the modified chitin can bind more than one MB species to fulfil the value of n higher than 1 [45].

Further confusion appeared on the proposed structure of chitin [45] which contained more $-CH_3$ group than the well accepted structure of chitin in literature, viz. Doğan et al. [47] and Santosa et al. [48]. Unfortunately, this difference was left without any explanation. Moreover, close inspection of the structure of MB provided in the paper of Franco et al. [45] showed that the MB was drawn as positively charged species with the presence of a negative charge on the one of the nitrogen atoms in the side groups of MB. It is surely unrealistic since all the resonance structures that may be drawn for MB only contain positive charge (see Fig. 6).

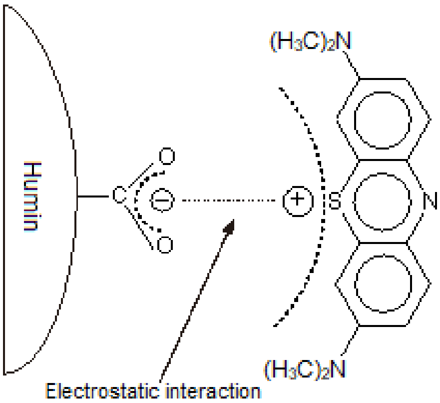

Fig 7. The most reasonable interaction between humin sorbent and cationic methylene blue (MB)

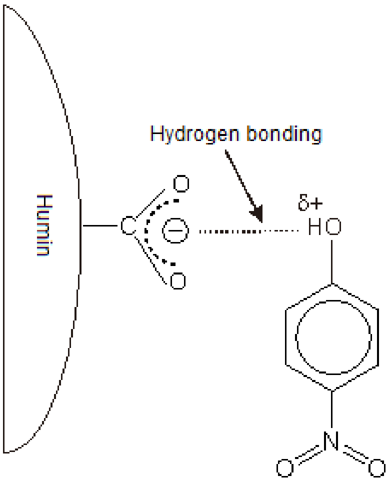

Fig 8. The most reasonable interaction between humin sorbent and *p*-nitrophenol (*p*-NP)

A previous study suggested that the N-acetyl group ($-NHCOCH_3$) on chitin was involved in a conjugation to form $-NHCOH=CH_2$ [48]. This conjugation weakens the affinity of O atom in the N-acetyl group to metal cation and yields the N atom as the stronger site in binding metal cation. The possibility of this conjugation was not considered by Franco et al. [45], so they still proposed that O atom in the N-acetyl group was the main receptor site for the positively charged MB.

An electrostatic interaction has also been proposed for the adsorption of MB on tannin component of sumac leaf at pH 5.0 [49]. The tannin employed its deprotonated phenolic-OH groups in binding the positively charged MB. However, it is hard to rationalize that the phenolic-OH groups of tannin have already been deprotonated at pH 5.00. They are commonly deprotonated at medium pH values much higher than 5.00. As occur to humic acids [50], it is more reasonable to deduce that –COOH, instead of the phenolic-OH, should be the deprotonated functional groups at pH 5.0.

Unlike MB, *p*-NP may exist as neutral and negative species depending on the medium pH. Since the sorption of *p*-NP in this study is done at medium pH 7.00 which is lower than the pKa value of *p*-NP (7.15), so the *p*-NP is present dominantly as neutral species.

Due to a concept of resonance and induction effect from the electron-withdrawing $–NO_2$ group, hydrogen on the –OH group of neutral *p*-NP is highly acidic. As a result, this acidic hydrogen will be the most suitable site for the interaction of neutral *p*-NP and the ionized –COOH group ($–COO^-$) of humin sorbent through the formation of hydrogen bonding (Fig. 8). The importance of this type of hydrogen bonding was also observed for the sorption of $AuCl_4^-$ on humin [11] and *p*-NP on Brazilian peat soil [46]. For the sorption of $AuCl_4^-$ on humin, the hydrogen bonding occurred between the acidic hydrogen atom of –COOH group of humin sorbent and one of the chloride atoms of $AuCl_4^-$ [11]. In the case of the sorption of *p*-NP on Brazilian peat soil, the hydrogen bonding was not specifically claimed to occur between $–COO^-$ of peat soil and acidic hydrogen of –OH group of *p*-NP [46].

The interaction model between *p*-NP and humin has never been reported in the literature, but that between phenols and active carbons has frequently studied [17]. Among several interaction models that were proposed between *p*-NP and active carbons, the hydrogen bonding has never been exclusively pointed out.

■ CONCLUSION

It was confirmed that humin derived from peat soil had high performance for the sorption of MB and *p*-NP from aqueous solution. Such sorption has been examined under acidic to alkaline medium conditions, with maximum sorption being observed at pH 6.20 and 7.00 for MB and *p*-NP, respectively. At this pH giving maximum sorption, attachment to $–COO^-$, as the deprotonated product of –COOH group, through electro static interaction was the most reasonable mechanism for the sorption of positively charged MB from aqueous solution. In the case of *p*-NP, its sorption was governed by hydrogen bonding between $–COO^-$ of humin sorbent and the acidic hydrogen on the –OH group of *p*-NP. A literature survey showed that neither sorption mechanism nor sorption performance of humin for MB and *p*-NP has ever been investigated yet.

The dominance of $–COO^-$ as the main active site on the sorption of MB and *p*-NP indicated that the surface of humin sorbent was energetically uniform and therefore the sorption data of both MB and *p*-NP on humin sorbent followed better the Langmuir than the Freundlich isotherm model. The Langmuir's sorption capacity for MB (0.19 mmol/g) was smaller than that for *p*-NP (0.26 mmol/g), while the sorption energy for MB (32.92 kJ/mol) was higher than that for *p*-NP (27.27 kJ/mol). The stronger attachment of MB on humin sorbent was in accordance with the aforementioned prediction that MB was bound by electrostatic interaction, while *p*-NP was attached by hydrogen bonding.

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