Synthesis and utilization of chitin–humic acid hybrid as sorbent for Cr(III)

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Abstract

New types of hybrid material have been synthesized by using four different methods of immobilization of humic acid (HA) on chitin. The most stable hybrid material toward the change of medium acidity was then utilized as sorbent for Cr(III).

The HA was extracted from peat soil of Gambut District, South Kalimantan, Indonesia, using the recommended procedure of International Humic Substances Society (IHSS), while the chitin was isolated from crab shell waste through deproteinization using 3.5% (w/v) NaOH and followed by removal of inorganic impurities using 1 M HCl. The four methods of immobilization of HA on chitin were (i) Method A: chitin powder (4 g) was gently poured into the stirred solution of 0.4 g HA in 40 mL of 0.01 M NaOH. After overnight stirring, the solid was separated, washed with water, and dried in oven at 70 °C.

(ii) Method B: gelatinous chitin (40 g) in 250 mL of 0.5 M HCl was reacted with HA (4 g) in 500 mL of 0.5 M NaOH and aged for 24 h. The product was washed with water and dried.

(iii) Method C: HA powder (0.5 g) was mixed with the stirred gel of chitin (2.5 g) in 60 mL of CaCl2 saturated methanol and the mixture was then washed with the mixed solution of 25 mL of 2 M sodium citrate and ethylene glycol 1:1. The solid was separated, washed with water, and dried.

(iv) Method D: the solution of HA (0.056 g) in 10 mL of 0.01 M NaOH was reacted with the gel of chitin (0.2 g) in 10 mL of CaCl2 saturated methanol. After 24 h stirring, the solid was separated from the reaction medium, washed with the mixed solution of 2 M sodium citrate and ethylene glycol 1:1, and followed by washing with water and drying. Parameters investigated in this study consisted of the stability test of the immobilized HA, as well as the rate constant (k1), capacity (b), and energy (E) of sorption as well as the rate constant of desorption (k−1). The k1 and k−1 were determined according to a kinetic model of first order sorption reaching equilibrium, while the b and E were determined according to the Langmuir isotherm model.

Compared to HA, Methods, A, C, and D; Method B produced the most stable immobilization of HA on chitin. The hybrid material (Chitin–HA) synthesized through Method B was stable in the acidity range that equivalent to pH 2.0–11.0. At the acidity giving maximum sorption, i.e. pH 5, the presence of immobilized HA on the Chitin–HA enhanced more than three times the k1 and k−1, i.e. from 0.057 min−1 and 8.51 × 10−4 (min−1) (mol/L) for chitin to 0.183 min−1 and 3.27 × 10−3 (min−1) (mol/L) for the Chitin–HA. On the contrary, the presence of HA on Chitin–HA only gave small increase on b and small decrease on E. The values of b and E for Cr(III) on chitin were 1.45 × 10−2 mol/g and 23.12 kJ/mol, respectively, while those on Chitin–HA were 1.78 × 10−2 mol/g and 19.95 kJ/mol, respectively.

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1. Introduction

Humic substances are a natural occurring organic compound ubiquitously spread-out in terrestrial and aquatic environments. It is commonly differentiated into humic acid (HA), fulvic acid (FA), and humin [1]. Humic acid is the fraction of humic substances that is insoluble in water under acid condition (pH ≤ 2.0), but becomes soluble at greater pH. Fulvic acid is the fraction that is soluble in water under all pH condition, and humin is the fraction that is insoluble in water at any pH value.

In term of capacity and rate of sorption, HA is a very good sorbent for various metal cations. This is why that in
context of environmental preservation, the high ability of HA in binding metal cations is a primary concern. Compared to the commonly used sorbent such as active carbon [2,3], bentonite [4,5], and metal oxides [6,7], HA generally possesses higher capacity and energy of sorptions, and it has also faster sorption for metal cations. Unfortunately, the existence of HA as a solid material for binding pollutant can only be maintained at the medium pH 2 or lower [1,8]. At medium acidity with the pH higher than 2, HA gradually dissolves and its rate of dissolution reaches maximum at pH 5. At pH 7, approximately 90% of HA has already dissolved [8].

Realizing the stability of solid HA as sorbent can only be maintained at medium pH 2 or lower, many efforts have been conducted to stabilize it through various methods of immobilization. Tombacz et al. [9] interacted HA and alumina. This interaction was only stable at the medium pH range of 4–10. Other kinds of aluminum and iron oxides have also been tried to be associated with HA [10]. All of the aluminum and iron oxides (goethite, hematite, gibbsite, and bochmite) could only give stable association at pH range of about 7.0–8.0.

For many purposes, semiconductors such as TiO2 and ZnO have been used together with HA. From the work of Selli et al. [11], it was clear that ZnO was only stable at medium pH 7–10, and another result using TiO2 [12] showed that the stability of the semiconductor of TiO2 was only in the pH range of 3–7. These evidences clearly indicate that both ZnO and TiO2 are not the proper candidates for the support material of HA.

Compared to the oxides described above, chitin possesses higher stability towards the change of acidity [13,14]. We observed that chitin isolated from Indonesian waste crustacean shell contained N-acetyl group in two different chemical forms of –NHC(O)CH3 and –NHC(O–)CH2 [15]. This functional group may interact through condensation reaction with carboxyl group of HA leading to stable immobilization of HA on chitin.

Our previous study revealed that HA could be immobilized on chitin through the reaction between alkaline solution of HA and gelatinous chitin in HCl to form Chitin–HA hybrid [16]. The immobilized HA on the Chitin–HA hybrid was stable in the medium acidity range that equivalent to pH 2.0–11.0. In this study, other Chitin–HA hybrids are further synthesized using other methods, their stability toward the change of medium acidity is investigated and then compared with the stability of the previously synthesized Chitin–HA hybrid [16], and the most stable Chitin–HA hybrid is then utilized as sorbent for Cr(III). The performance of the sorbent is evaluated based on the data of energy, capacity, and rate constant of sorption as well as the rate constant of desorption.

2. Materials and methods

2.1. Materials

Reagents used in this study are analytical grade originally produced by E. Merck Co Inc. (Germany), and then treated and prepared in order to be suitable for the real experiments. The prepared reagents consist of: (1) reagents for isolation of HA from peat soil, i.e. 1 M and 6 M HCl, 0.1 M NaOH, mixed solution of 1 M HCl and 1 M HF (1:1); Dowex 50-X8 cation exchange resin; (2) stock solutions of 1000 ppm Cr(III) from Cr(NO3)3 crystal, (3) standard solutions for preparing standard curve for the determination of Cr(III) using atomic absorption spectrophotometer (AAS). These standard solutions are prepared by diluting the stock solutions; and (4) buffer solutions at pH 4.0, 7.0, and 10.0 produced by Fischer Scientific Co. for pH meter calibration; (5) reagents for isolation of chitin, i.e. 3.5% (w/v) NaOH and 1 M HCl; (6) reagents for functional group analysis of HA, i.e. 0.1 M Ba(OH)2, 0.5 M HCl, 0.5 M Ca(CH3COO)2, and 0.1 M NaOH and (6) methanol, sodium citrate, ethylene glycol, HCl and NaOH solutions at appropriate concentrations were also prepared for the preparation of sorbent and/or the determination of HA content in each Chitin–HA hybrid.

2.2. Methods

The methodology in carrying the experimental activities are described in the order of: (i) sampling and sample preparation, (ii) isolation and characterization of HA, (iii) quantitative analysis of functional groups of HA, (iv) isolation and characterization of chitin, (v) preparation of Chitin–HA hybrid through immobilization of HA on chitin and its stability test and characterization, and (vi) the determination of total amount of HA contained in Chitin–HA hybrid.

In the application of chitin and Chitin–HA hybrid to absorb Cr(III), four parameters, i.e. sorption and desorption rate constants, as well as capacity and energy of sorption were determined.

2.3. Sampling and sample preparation

Peat soil as source of HA was obtained from Gambut District, South Kalimantan, Indonesia. The peat soil was taken using a Teflon pipe dipped in weak and partly submerged peat soil. Peat soil trapped inside the Teflon pipe was pouring out and collected in a black plastic bag. After transportation and returning to the laboratory, peat soil was dried in room condition under the flow of nitrogen gas to prevent oxidation by oxygen in the atmosphere.

Crustacean shell waste as a source of chitin was collected from traditional market and sea-food restaurant in Semarang, Central Java, Indonesia. The crustacean shell was dried in oven at 60 °C and then crushed and sieved to the size of 80 mesh or smaller.

2.4. Extraction, purification, and quantitative analysis of the functional groups of HA

Extraction of the HA was performed according to the recommendation of the International Humic Substances
Society (IHSS) [17]. Toward the extracted HA, two kinds of analysis were conducted to quantify its main functional groups. Those kinds of analysis were the analyses of total acidity (carboxyl and phenolic-OH groups) and carboxyl group that were determined by barium and calcium acetate, methods, respectively [1]. From those data, phenolic-OH group is then calculated from the difference between total acidity and carboxyl group.

2.5. Isolation and characterization of chitin

The prepared crustacean shell was stirred for 2 h in 3.5% (w/v) NaOH at temperature 65 °C to dissolve protein. The ratio between the weight of crustacean shell (g) and the volume of NaOH (mL) is 1:10. After cooling to room temperature, the residue was separated and washed with aquadest to neutral. Minerals within the residue was removed by refluxing the residue in 1 M HCl for 30 min. After this reflux, the residue was expected to contain chitin only. The chitin was then separated, washed with aquadest to neutral, and dried at 60 °C in oven to constant weight. The same as HA, the characterization of chitin was performed by FT-IR Spectroscopy. From the FT-IR spectra, the functional group of chitin was identified and the deacetylation degree was calculated using an equation proposed by Domszy and Robert [18]. In addition, the analysis of total nitrogen (N) using Kjeldahl method was also performed.

2.6. Preparation of Chitin–HA hybrid through immobilization of HA on chitin and its stability test and characterization

Four methods of immobilization of HA on chitin were conducted, i.e. (i) Method A: chitin powder (4 g) was gently poured into the stirred solution of 0.4 g HA in 40 mL of 0.01 M NaOH. After overnight stirring, the solid was separated, washed with water, and dried in oven at 70 °C. (ii) Method B: gelatinous chitin (40 g) in 250 mL of 0.5 M HCl was reacted with HA (4 g) in 500 mL of 0.5 M NaOH and aged for 24 h [16]. The product was washed with water and dried. (iii) Method C: HA powder (0.5 g) was mixed with the stirred gel of chitin (2.5 g) in 60 mL of CaCl2 saturated methanol and the mixture was then washed with the mixed solution of 25 mL of 2 M sodium citrate and ethylene glycol 1:1. The solid was separated, washed with water, and dried. (iv) Method D: the solution of HA (0.056 g) in 10 mL of 0.01 M NaOH was reacted with the gel of chitin (0.2 g) in 10 mL of CaCl2 saturated methanol. After 24 h stirring, the solid was separated from the reaction medium, washed with the mixed solution of 2 M sodium citrate and ethylene glycol 1:1, and followed by washing with water and drying.

For every hybrid of Chitin–HA, the stability test of the HA contained in the hybrid was performed as follow [16]. 500 mg of the hybrid material was added to a series of 50 mL of distilled waters and the acidity of the waters was then adjusted to pH of 1.0, 3.0, 5.0, 7.0, 9.0, 11.0, and 13.0 using either HCl or NaOH solution. The mixtures were stirred for 30 min and followed by standing for 24 h. After separating supernatant from the solid, the content of dissolved HA in supernatant was determined spectrometrically at 400 nm using standard addition method.

2.7. Sorption of Cr(III)

2.7.1. Effect of medium acidity

First, a series of 15 mL of 50 mg/L Cr(III) solutions was prepared and the acidity was adjusted to pH 2.0, 4.0, 6.0, 8.0, and 10.0 by adding HCl or NaOH solution. Into every Cr(III) solution, 10 mg of sorbent (chitin or Chitin–HA) was poured and then stirred for 2 h. After filtering through 0.45-μm membrane filter, the concentrations of Cr(III) in the supernatants were analyzed by using AAS. Sample and blank solutions were analyzed under the same condition. The amount of Cr(III) sorbed was considered to be the difference between the initial amount and the amount remaining in the reacting solution.

2.7.2. Kinetics

The kinetic experiments were carried out in a batch-type reactor using a 50-mL Erlenmeyer in a water bath at 25 ± 0.1 °C. The effective volume of the solution of the reacting suspension was 10 mL, the initial metal ion concentration was 100 mg/L, the acidity was adjusted at pH 5.0, and to each solution 10 mg chitin or Chitin–HA was added and then stirred continuously. At a selected time period, the sample was immediately filtered through 0.45-μm membrane filter and the concentration of Cr(III) remaining in the supernatant was analyzed using AAS. Sample and blank solutions were analyzed under the same condition. The amount Cr(III) sorbed was considered to be the difference between the initial and the remaining amount of Cr(III) in the reacting solution. From the data obtained, the value of sorption and desorption rate constants were then calculated based on the assumption that the sorption obeyed the first order sorption reaching equilibrium that has been described elsewhere [19].

2.7.3. Capacity and energy

The experiments were also conducted using a batch-type reactor at 25 ± 0.1 °C. As much as 10 mg of chitin or Chitin–HA was interacted with and stirred in 10 mL of solutions containing the various concentrations of 50, 100, 150, 200, 250, 300, 500, and 1000 mg/L Cr(III) for as long as 2 h. After separating the supernatants, the concentrations of Cr(III) in the supernatant were determined using AAS. Under the same condition with the sample solution, the blank solution was also analyzed. Based on the data obtained, the capacity (b) and equilibrium constant (K) of sorption was calculated based on the Langmuir isotherm sorption model, and the energy (E) of sorption was then calculated from the equation of

$$E = RT \ln K$$

[20,21].
3. Results and discussion

3.1. Extraction, purification, and quantitative analysis of the functional groups of HA

The extraction and purification procedure recommended by IHSS was able to separate pure HA with the efficiency of 3.50% (w/w). Before the extraction, the ash content of peat soil was 55.63% (w/w), and after extraction, the ash content decreased to 6.80% (w/w). The further decrease to 1.47% (w/w) on the ash content was obtained after purification.

HCl and HF mixed solution and a cation exchange resin were employed in the purification step of HA. This mixed solution and cation exchange resin are, therefore, able to release HA from its interaction with metal and other impurities such as silicon since peat soil in the environment naturally interacts with minerals like clay mineral to form humic–metal–clay complex [1].

The potentiometric titration revealed that carboxyl (COOH) and phenolic OH were the main functional group possessed by HA. Their concentrations were 1688 mmol/kg for COOH and 622 mmol/kg for phenolic OH.

3.2. Isolation and characterization of chitin

In this study, the chitin was isolated through deproteination and then followed with demineralization of marine crustacean shell. The isolated chitin was then characterized using FT-IR spectroscopy with the result is presented in Fig. 1.

As presented in our previous paper [16], the chitin that in this study was isolated using slightly different isolation procedure with the isolation procedure used in the previous paper [16] showed main absorption bands at 3450, 3270, 3100, 2900, 2890, 1660, 1630, 1560, 1415, 1377, and 1070 cm⁻¹. Absorption band at 3450 cm⁻¹ was characteristic for –OH, and that at 3270, 3100, and 1630 cm⁻¹ was for N–H stretching, N–H symmetric stretching, and N–H bending, respectively [22]. Carbonyl (C=O) stretching of acyl group (CH₃C=O) appeared at 1660 cm⁻¹, while asymmetric and symmetric bending of C–CH₃ appeared at 1415 and 1377 cm⁻¹, respectively. The presence of bonding between N from acetamide moiety and C from acyl group was shown by absorption band at 1560 cm⁻¹ that was characteristic for N–C stretching. The other absorption bands at 2900, 2890, and 1070 cm⁻¹ were characteristic for asymmetric and symmetric stretching of C–H of CH₂, and stretching of C–O, respectively [22].

From the FT-IR spectra of the isolated chitin (Fig. 1), the resulted deacetylation degree calculated using an equation proposed by Domszy and Robert [18] was 45.86%, while the analysis of total nitrogen (N) using Kjeldahl method gave the concentration of 4.63%.

3.3. Preparation of Chitin–HA hybrid through immobilization of HA on chitin and its stability test and characterization

All methods of immobilization of HA on chitin conducted here produced the change of color from white (the color of chitin) to brown or light brown. After rinsing with and immersing in water for more than 24 h, Method B is the only method of immobilization which yields the most stable color of the material. It is an indication that the HA immobilized according to Method B is stable enough toward dissolution.

Stability test performed to the all Chitin–HA hybrids obtained from the all immobilization methods confirmed the indication above (Fig. 2). This stability test was done after determining the amount of HA contained in Chitin–HA. The determination of the amount of HA contained in Chitin–HA was done as follow [16]: 100 mg of Chitin–HA was dissolved in 50 mL of 0.05 M NaOH to result clear solution. By using standard addition method, the content of HA released from the sorbent to the solution was then determined using ultraviolet–visible spectrometer at wavelength of 400 nm. The determination gave the content of HA in Chitin–HA prepared by Methods A, B, C, and D as much as 0.87%, 1.01%, 0.06%, and 0.12% (w/w), respectively. This content was then used as a basis to calculate the stability of immobilized HA in every Chitin–HA hybrid at various medium acidities.

As can be seen in Fig. 2, compared to HA, Methods A, C, and D; Method B produced the most stable immobilization of HA on chitin. While the stability of HA and hybrid materials synthesized through Methods A, C, and D continuously decreased from pH 1.0 to lower medium acidity,
the Chitin–HA hybrid synthesized through Method B was stable in the acidity range equivalent to pH 2.0–11.0.

Characterization using FT-IR toward the Chitin–HA hybrid obtained from Method B generated spectra that is very similar to the spectra of chitin (Fig. 1). The only difference between the two spectra was the presence of absorption band at 2586 cm$^{-1}$ and the relatively longer absorption band at 1628 cm$^{-1}$ after the immobilization.

As described in the previous paper [16], the absorption band at around 2600 cm$^{-1}$ was the asymmetric stretching of O–H from OH group in –COOH. Since chitin contains no –COOH group, the FT-IR spectra of chitin lack of the absorption band at 2600 cm$^{-1}$, but after HA stacks on chitin, the resulted material contains –COOH group and therefore, the absorption band at 2586 cm$^{-1}$ appears.

Both chitin and HA possessed absorption band at around 1628 cm$^{-1}$ (Fig. 1). As described before, the absorption band at around 1628 cm$^{-1}$ for chitin was attributed by N–H bending, while that for HA was characteristic for the stretching of aromatic C=C and stretching of C=O in COO$^-$ [16]. It is likely that the enhancement on the absorption band at 1628 cm$^{-1}$ is because of the presence of HA on chitin.

3.4. Sorption of Cr(III)

3.4.1. Effect of medium acidity

The amount of sorbed Cr(III) was highly affected by medium acidity (Fig. 3). With decreasing medium acidity from pH 2 to pH 4, the sorbed Cr(III) on chitin sharply increased, relatively constant at pH 4.0–5.0 and at low medium acidity (pH > 5), the sorbed amount of Cr(III) again decreased rapidly. The similar pattern is shown by profile of the sorbed Cr(III) on the Chitin–HA. The maximum sorption of Cr(III) on Chitin–HA was also observed at pH around 5.0.

At high medium acidity (pH ≤ 3.5), Cr(III) is the most abundance Cr(III) species in the solution [23], but this Cr(III) must compete with H$^+$ in occupying the active sites of sorbents. As a result, the sorption of Cr(III) at low pH was small. Decreasing H$^+$ amount in the solution that means the decreasing of the amount of the competitor, leads to the increase of the sorbed Cr(III). This evidence can be observed at medium acidity from pH 3.5 to pH 5. At low medium acidity (pH > 6.5), Cr(III) species are predominantly in the form of insoluble Cr(OH)$_3$. This is why that the sorption of Cr(III) decreased with increasing pH after its maximum at pH around 5.0.

3.4.2. Kinetics

Although the sorption of Cr(III) on both chitin and Chitin–HA hybrid was initially rapid and then slower, the presence of HA on Chitin–HA likely enhanced the sorption rate (Fig. 4). The rapid sorption for Cr(III) on chitin occurred at the first 30 min, while that on Chitin–HA at the first 20 min.

Applying a kinetic model of first order sorption reaching equilibrium with the mathematical expression as shown below [19], linear relationship between ln($C_0/C_A$) vs. t/ $C_A$ was obtained with correlation coefficient ($R^2$) = 0.9559 and 0.9998 for the sorbents of chitin and Chitin–HA, respectively (Table 1):

$$\ln \left(\frac{C_0}{C_A}\right) = k_1 \frac{t}{C_A} + Q$$
The presence of HA on chitin will increase both ion like Cr(III). As a result, from the point of view of equi-
must compete with water in attracting the hard metal cat-

Table 1 Sorption ($k_1$) and desorption ($k_{-1}$) rate constants, and the correlation coefficient ($R^2$) of the plot of ln($C_{mol}/C_A$)/$C_A$ vs. $t/C_A$ for the sorption of Cr(III) on chitin and Chitin–HA hybrid

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Sorption–desorption parameters</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitin</td>
<td>$k_1$ = 0.057 min$^{-1}$, $k_{-1}$ = $8.51 \times 10^{-4}$ (mol/L)</td>
<td>0.959</td>
</tr>
<tr>
<td>Chitin–HA</td>
<td>$k_1$ = 0.183 min$^{-1}$, $k_{-1}$ = $3.27 \times 10^{-3}$ (mol/L)</td>
<td>0.9998</td>
</tr>
</tbody>
</table>

where $C_{0b}$ is the initial concentration of metal ion, $C_A$ is the remaining concentration of metal ion after sorption at $t$ sorption time, $k_1$ is sorption rate constant, $Q = k_1/k_{-1}$ is sorption–desorption constant and $k_{-1}$ is desorption rate constant.

Fig. 4. Effect of contact time on the sorption of Cr(III) on chitin and Chitin–HA hybrid.

As can be predicted from Fig. 4 that the presence of HA on chitin may enhance the sorption rate. This prediction was confirmed, i.e. the sorption rate constant ($k_1$) increased 3.21 times, from 0.057 for the sorbent of chitin to 0.183 min$^{-1}$ for the sorbent of Chitin–HA. Like $k_1$, the desorption rate constant ($k_{-1}$) also increased 3.84 times, i.e. from $8.51 \times 10^{-4}$ for the sorbent of chitin to $3.27 \times 10^{-3}$ (min$^{-1}$) (mol/L) for the sorbent of Chitin–HA. Although the presence of HA on chitin adds the amount of active site suitable for sorption of metal cation especially for relatively hard metal cations [11], but the active site must compete with water in attracting the hard metal cation like Cr(III). As a result, from the point of view of equi-
lumbration sorption, the additional active site due to the presence of HA on chitin will increased both $k_1$ and $k_{-1}$. The sorption rate enhancement for metal cations other than Cr(III) due to the presence of HA on chitin and silica gel was also observed in previous studies [14,25].

3.4.3. Capacity and energy

The Langmuir isotherm sorption model with the mathematical expression given below was used to determine the capacity ($b$) and equilibrium constant ($K$) of sorption, and the energy ($E$) of sorption was then calculated according to the equation $E = RT\ln K$ [20,21]:

$C = \frac{1}{m} + \frac{C}{bK}$

where $C$ is the concentration of metal ion remaining in solution at equilibrium, $m$ is sorbed metal ion on 1 g sorbent, $K$ is equilibrium constant of sorption and $b$ is sorption capacity.

The presence of HA slightly increases $b$, but reversely decreases $E$ (Table 2). The similar evidence was observed for Ni(II), the presence of HA on chitin caused $b$ to increase slightly, while $E$ to decrease slightly [19]. As stated before that the presence HA on chitin increases the active site which mainly in the form of carboxyl group. The carboxyl group is likely not strong enough to compete with water in attracting Cr(III).

Table 2 Capacity ($b$), energy ($E$), and equilibrium constant ($K$) for the sorption of Cr(III) on chitin and Chitin–HA hybrid

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Sorption parameters</th>
<th>$K$ (mol/L)$^{-1}$</th>
<th>$E$ (kJ/mol)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chitin</td>
<td>$b$ = 1.45 $10^{-5}$ mol/g</td>
<td>11295</td>
<td>23.12</td>
<td>0.9814</td>
</tr>
<tr>
<td>Chitin–HA</td>
<td>$b$ = 1.78 $10^{-5}$ mol/g</td>
<td>3140</td>
<td>19.95</td>
<td>0.9987</td>
</tr>
</tbody>
</table>

References