Removal of methyl orange dye and copper (II) ions from aqueous solution using polyaniline-coated kapok (Ceiba pentandra) fibers

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ABSTRACT

Hollow tubular structured kapok fibers (Ceiba pentandra) were coated with polyaniline (PANI) molecules using an in situ oxidative polymerization technique. The tubular morphology of the kapok fibers was retained after PANI coating. The Fourier transform infrared (FT-IR) spectrum of the PANI-coated kapok fibers illustrated the vibration modes associated with the presence of PANI molecules. The PANI-treated kapok fibers achieved complete wettability with water molecules (zero water contact angle) from initially being highly hydrophobic (contact angle $\approx 120^\circ$). In the present work, the removal of contaminants such as methyl orange dye and Cu(II) from aqueous solution using polyaniline-coated kapok fibers was investigated. Isotherm studies show that the removal of methyl orange dye ($R^2 \geq 0.959$) and Cu(II) ($R^2 \geq 0.972$) using PANI-coated kapok fibers follow the Langmuir isotherm model with maximum sorption capacities determined to be 75.76 and 81.04 mg/g, respectively. Based from thermodynamic studies, the sorption of methyl orange dye and Cu(II) are endothermic, feasible and spontaneous. Furthermore, kinetic studies show that the both processes follow a pseudo-second-order model, implying that the rate-determining step is chemisorption.

Key words | adsorption, anionic dye, metal ion, microtubes, pseudo-second-order model

INTRODUCTION

Natural fibers with hollow microtubular structure such as Platanus acerifolia seed fibers, populus seed fibers, milkweed fibers and kapok fibers have been the subject of various researches (Rengasamy et al. 2011; Likon et al. 2013; Siswoyo et al. 2014). This is because natural fibers are abundant, renewable, cheap and lightweight with high surface area-to-volume ratio. Natural fibers have been commonly used as substrate or template of different functional materials (Zheng et al. 2014; Agcaoili et al. 2017; Cao et al. 2017). However, free-standing or template-free functional materials have the tendency to agglomerate, which would minimize the surface contact area between the functional materials and aqueous environment. In order to minimize aggregation, functional material can be immobilized onto a substrate or template. This immobilization also results to the strategic distribution of the material over a specific surface area.

Kapok fibers, which are categorized as lignified organic seed fiber, are also characterized by its hollow structure with an oval cross-section, thin wall (0.8–1.0 $\mu$m in wall thickness and 8–10 $\mu$m in diameter), wax-covered smooth surface and porosity of more than 80% (Mwaikambo & Bisanda 2013; Chung et al. 2008; Xiang et al. 2013). Moreover, the fibers are considered to be excellent template material due to their natural microtubular structure. The excellent capacity of kapok fibers to separate oil, chemical oxygen demand (COD) and turbidity are attributed to its hydrophilic–oleophilic surface (Rahmah & Abdullah 2009). However, the hydrophobic characteristics of kapok limit the possible application as sorbent in aqueous media. In order to modify the surface characteristics, kapok fibers can be subjected to chemical or physical treatment.

Polyaniline (PANI), which is a type of conjugated polymer, has relatively good thermal and environmental
stability, and high electrical conductivity (Anand et al. 1998; Gospodinova & Terlemezyan 1998; Eftekhar et al. 2017). Moreover, it is cost-effective and non-toxic. Emerladine salt, which is one of the useful forms of PANI, is characterized by its highly protonated form and relatively high conductivity, which can offer different possible applications such as fabrication of anti-electrostatic materials, conductive adhesive, conductive ink, and conductive paint (Xu et al. 2015). PANI molecules are rich in reactive nitrogen-based groups such as amino and imine groups, which becomes advantageous in serving as binding sites for sorption applications. However, application of pure PANI is limited due to its low surface polymer area. Modification of PANI into nanomaterials or composite materials helps overcome this limitation and improve other physical and chemical properties. PANI and PANI-incorporated based materials have been developed in the removal of various contaminants such as pigments (Ahmed et al. 2016; Laabd et al. 2016; Sharma et al. 2016) and heavy metals (Daraei et al. 2012; Li et al. 2014; Liu et al. 2016).

Copper (Cu), which is considered an inorganic pollutant, is generated by the pulp and paper, and metal plating industries (Volesky & Holan 1995). It is also found in fungicides, insecticides, and fertilizers (Volesky & Holan 1995). It is a well-known indispensable trace element that plays a vital role in enzymatic activities (Xie et al. 2017). However, high uptake of Cu can prove to be toxic that can cause various illnesses such as autism, tardive dyskinesia, hepatic and renal dysfunctions, gastrointestinal irritation, and hypertension (Pfeiffer & Mailloux 1987). Methyl orange (MO), which is a type of anionic azo dye, is characterized by its complexity of organic components, stable chemical quality, resistance to microbial degradation and high chromaticity (Xin et al. 2015). MO dye is commonly utilized by various food industries, pharmaceuticals, textiles, paper mills and printing shops (Hassandazeh-Tabrizi et al. 2016). The presence of dyes in water bodies leads to production of hazardous intermediates after undergoing oxidation, which are toxic to aquatic organisms (Li et al. 2017). In addition, coloring material in the water system reduces light penetration that decreases the photosynthetic activity of aquatic organisms (Mittal et al. 2007). Dyes contained in wastewater effluents have been determined to have caused health problems in humans due to their mutagenic and carcinogenic effects (Wang et al. 2005). Sorption is one of the most practical treatment methods, especially if large volume of effluent is being considered. The process has several advantages such as economic feasibility, simplicity of design, ease of operation, and high efficiency without production of sludge and other harmful by products (Unnithan & Anirudhan 2007; Fu & Wang 2011). Previous studies utilized organic and natural sorbents for the removal of Cu(II) and MO, such as surfactant-modified silkworm exuviae (Chen et al. 2011), graphene oxide (Robati et al. 2016), goethite (Munagapati et al. 2017), polycrystalline-coated kapok (Agcaoili et al. 2017), chemically-modified orange peel (Feng et al. 2009), peanut hull (Zhu et al. 2009), and tartaric acid-modified rice husk (Wong et al. 2003).

The main objective of the present work is to evaluate the polyaniline-coated (PANI-coated) kapok fibers in the removal of Cu(II) and MO from aqueous solution under static conditions. The kapok fibers were coated with PANI molecules using an oxidative-type in-situ technique. Specifically, this study aims to characterize the coated fibers using Fourier transform infrared (FT-IR) spectroscopy, water contact angle measurement and scanning electron microscopy (SEM). Equilibrium data were analyzed using isotherm models including Langmuir, Freundlich and Dubinin-Radushkevich equations. In addition, experimental data were fitted using kinetic equations and thermodynamic parameters, including ΔG°, ΔH° and ΔS°, were determined.

**EXPERIMENTAL**

**Synthesis of polyaniline-coated kapok fibers**

In 100 mL distilled water, 1.20 g NaClO₂ (80% AR, Sigma Aldrich) was dissolved with 1.90 mL glacial CH₃COOH (99.7%, AR, Macron Fine Chemical). Then, 1.5 g kapok fibers were immersed in the solution and the mixture was stirred at 700 rpm for 60 min at 90 °C. The treated fibers were washed with distilled water and dried at 60 °C.

The coating process involves dissolution of 2.0 g aniline (95%, AR, Loba Chemie) in 66.0 mL of 1.0 M HCl (37% fuming, Sigma Aldrich) and immersing 40 g kapok fibers in the solution. Then, mixture was stirred for 30 min in an ice bath. On the other hand, the oxidant solution was prepared by mixing 4.0 g (NH₄)₂S₂O₈ (98%, AR, HIMEDIA) in 16.0 mL of 1.0 M HCl placed in an ice bath. Then, the oxidant solution was added in a dropwise manner into the kapok-aniline mixture. Then, the mixture was stirred for an hour and left to stand for 16 h at 25 °C. The treated polyaniline-coated fibers were filtered and washed using distilled water until the supernatant became colorless. Then, the fibers were washed using ethanol (95%, AR, Ajaxfinechem), air dried for 24 h and dried in an oven at 60 °C for 24 h. The FT-IR spectra (Prestige-21 Shimadzu) of the kapok fibers...
were recorded with wavelength of 400–4,000 cm\(^{-1}\). Morphological characterization of kapok and modified kapok fibers was done using scanning electron microscope (JEOL JSM 5310).

**Sorption experiment**

Sorption experiments were carried out by adding 20 mL solution and a determined mass of PANI-coated kapok in a 125-mL Erlenmeyer flask that was agitated for 24 h. The effect of mass of PANI-coated kapok (20 to 50 mg) and pH of the solution (2.0 to 10.0) on the sorption capacity were determined. The adjustment of the pH solution was performed using 0.1 M HCl or NaOH.

Isotherm studies were performed where 30.0 mg PANI-coated kapok was added in 20.0 mL solution at different initial concentration (40 to 280 ppm) where aliquot was agitated for 24 h. The initial pH of the solution for Cu(II) and MO is pH 4.3 and 6.5, respectively. Then, the treated effluent was filtered and analyzed for residual contaminant.

For the thermodynamics experiments, 30.0 mg PANI-coated kapok were mixed in a 20 mL solution and agitated for 8 h at 90 rpm under varying temperature (25 to 70 °C). For kinetic studies, a mixture of 30.0 mg PANI-coated kapok and 20.0 mL solution was agitated using a shaker bath at pre-determined time intervals (0 to 24 h).

The residual MO concentration was analyzed using ultraviolet-visible spectrophotometer (UV-Vis 1700 Shimadzu, Japan) at \(\lambda = 464 \text{ nm} \). The quantitative analysis of Cu(II) was performed using an ICP-OES Perkin Elmer DV 2000 series. The sorption capacity at any time \(t\), \(q_t\) was calculated using Equation (1):

\[
q_t = \left( \frac{C_0 - C_t}{M} \right) \times V
\]

where \(V\) (mL) refers to the total volume of the solution, \(M\) (g) is the adsorbent mass, \(C_0\) (mg/L) and \(C_t\) (mg/L) are the initial concentration and residual concentration of contaminant, respectively.

**RESULTS AND DISCUSSION**

**Characterization of polyaniline-coated kapok fibers**

Figure 1(a) shows the FT-IR spectrum of the polymer-coated sample, while Table 1 summarizes the peaks of the spectrum with the corresponding interpretations. The presence of the peaks at 1,578 and 1,489 cm\(^{-1}\) refers to the strong presence of quinoid and benzenoid rings, respectively (Trčhova & Stejskal 2011). The peak at 1,300 cm\(^{-1}\) suggests the presence of amine group, which intermediates the two benzenoid rings as seen in the molecular structure of PANI emeraldine salt in Figure 2 (Trčhova & Stejskal 2011). The peaks at 1,404 and 1,146 cm\(^{-1}\) show the presence of positively charged imine group (iminium), which intermediates a quinoid ring and benzenoid ring (Trčhova & Stejskal 2011). The presence of iminium indicates that the PANI molecules are in the form of emeraldine salt, which is the protonated (doped) form of emeraldine base (Figure 1(b)). The downward peaks in the FT-IR spectrum such as 1,740, 1,420, 1,366, 1,231, 1,038 and 899 cm\(^{-1}\) are attributed to the different molecular vibrations of carbohydrate in the kapok fibers. Meanwhile, the peak at 1,632 cm\(^{-1}\) is attributed with the O-H bending of water molecules adsorbed in the kapok fibers.

The kapok fibers became hydrophilic after the treatment procedures as seen in Figure 1(c) and 1(d). The water contact angle of uncoated kapok fibers was around 120° (Figure 1(c)). Materials with water contact angle greater than 90° are considered hydrophobic. Hydrophobic materials repel water molecules on their surface, a condition that is not conducive for sorption in aqueous media. After the treatment processes, the water contact angle of the fibers reduced to zero (Figure 1(d)). Materials with a water contact angle less than 90° are considered hydrophilic. In addition, the zero value of the water contact angle implies that the fibers achieved complete wettability with water.
The fibers need to have complete wettability with water to be best used for sorption purposes in aqueous media.

Figure 2 shows the SEM micrographs of kapok fibers before and after coating with PANI. The kapok fiber has micro-tubular structure, having a lumen in the middle. The diameter of the fiber is estimated to be about 19.98 μm (Figure 2(a)). After coating, most areas of the kapok fiber were evenly coated with PANI. The coated areas appeared to have coarser structures compared to that of the uncoated areas. The coating thickness is estimated to be about 2.38 μm. Interestingly, the tubular structure of the fibers was still observed after coating with PANI molecules.

Effect of initial solution pH and mass of PANI-coated kapok

Mass of sorbent and initial pH of the solution are two essential parameters that would affect the operating costs of the wastewater treatment system. Based on Figure 3(a), increasing the mass of PANI-coated kapok from 20 to 30 mg led to an increase in sorption capacity from 50.27 to 57.85 mg/g, respectively. A higher mass of 30 mg would imply larger surface area and binding sites available to remove MO molecules from the solution. However, further increasing the mass of PANI-coated kapok to 50 mg resulted in a slight decrease in sorption capacity. This shows that aggregation of the PANI-coated kapok fibers may have occurred at higher dosages that would lead to lower surface area available for sorption and greater length for diffusional path of MO molecules (Jafari et al. 2018). In Figure 3(b), results illustrate that acidic solution (pH < 7.0) has better sorption capacity in comparison to basic solution. An acidic pH would indicate positively-charged surface of the sorbent that is due to the polaron/bipolaron sites (Zheng et al. 2015). The positively charged surface of the PANI-coated kapok would electrostatically interact with the negatively-charged sulfonate group (SO$_3$Na) present in MO dye.
Basic pH would imply that the emeraldine salt of PANI would be in its neutral form wherein the binding sites become deactivated and results in lower sorption capacities.

**Sorption isotherms**

Isotherm models are utilized to measure the sorption capacity of a sorbent in removing a certain contaminant. The equilibrium data were evaluated using isotherm models, such as Langmuir, Freundlich and Dubinin-Radushkevich (D-R) equations.

The Langmuir model assumes the formation of a monolayer sorption occurring on the sorbent surface where the binding sites are described as energetically homogenous (Zawani et al. 2009). Moreover, only one sorbate molecule can occupy an active site and there are no interactions occurring between sorbate molecules (Labidi et al. 2016). The linear form of the Langmuir model is given as Equation (2):

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}
\]

where \( q_e \) is the equilibrium quantity of adsorbate onto the adsorbent (mg/g), \( K_L \) is the Langmuir constant, and \( q_m \) is the maximum sorption capacity (mg/g) required to form a monolayer (Langmuir 1918).

The empirical Freundlich model assumes that a fraction of increase in the occupied sorption sites would result to a logarithmic increase in the sorption enthalpy, where the sorbent surface is heterogeneous in nature where physical forces are involved in the multilayer sorption (Freundlich 1906). The linear form of the Freundlich isotherm is provided as Equation (3):

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

where \( K_F \) is the Freundlich sorption coefficient that refer to the sorption capacity (mg/g) and \( 1/n \) is an empirical exponent referring to the sorption intensity (L/mg).

The D-R model was initially applied to describe the isotherm of sub-critical vapors in microporous solids, where van der Waals forces mainly govern the sorption system (Dubinin & Radushkevich 1947). The linear D-R equation is given as Equation (4):

\[
\ln q_e = \ln q_{D-R} - \beta \varepsilon^2
\]

where \( q_{D-R} \) refers to the theoretical D-R saturation capacity (mg/g), \( \beta \) is the D-R constant (mol²/kJ²) and \( \varepsilon \) is Polanyi potential (kJ/mol). The Polanyi potential can be computed using Equation (5):

\[
\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right)
\]

where \( R \) is the gas constant (8.3145 J/mol·K) and \( T \) is operating temperature (K). The mean free energy of sorption, \( E \) (kJ/mol) can be compute from the D-R constant as Equation (6):

\[
E = \frac{1}{\sqrt{2\beta}}
\]

The calculated isotherm parameters derived from Langmuir, Freundlich and D-R models are listed in Table 2. Based on the correlation coefficient values, Langmuir...
In the sorption system, thermodynamics parameters \( \Delta G^o \), \( \Delta H^o \), and \( \Delta S^o \) will help define the nature of the removal of MO and Cu(II) using PANI-coated kapok. The parameters can be calculated using Equations (7) and (8):

\[
\Delta G^o = -RT \ln K_D \tag{7}
\]

\[
\ln K_D = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{8}
\]

where \( T \) is the solution temperature (K), \( R \) is the universal gas constant (8.314 J/mol·K) and \( K_D \) is the Langmuir equilibrium constant, \( \Delta G^o \) refers to the Gibbs free energy (kJ/mol), \( \Delta H^o \) refers to the enthalpy (kJ/mol) and \( \Delta S^o \) refers to the entropy (kJ/mol·K).

Based from Table 3, the negative values of \( \Delta G^o \) under all temperature range studied imply that the sorption of MO and Cu(II) using PANI-coated kapok is feasible and spontaneous. In both sorption of MO and Cu(II), the values of \( \Delta G^o \) become more negative as temperature was increased, which indicates that sorption was more spontaneous and favored at higher temperature. The magnitude of \( \Delta G^o \) would serve as one of the criteria to determine between physisorption and chemisorption. When \( \Delta G^o \) values ranges from -20 to 0 kJ/mol, this refers to physisorption while \( \Delta G^o \) values from -80 to -400 kJ/mol would indicate chemisorption (Yu et al. 2001). Results show that sorption of MO and Cu(II) using PANI-coated kapok is governed by physical sorption. The values of \( \Delta H^o \) for the removal of MO and Cu(II) are positive, which indicate that the sorption process is endothermic. Moreover, the positive values of \( \Delta S^o \) for MO and Cu(II) suggest that sorption process lead to increased randomness at the solid-solution interface.

### Sorption kinetics

The kinetics of sorption, most importantly the kinetic rate constant, can be utilized in the design of the sorption system. Among the kinetic equations, the pseudo-first-order and pseudo-second-order equation of MO and Cu(II) were investigated. The pseudo-first-order model, otherwise known as the Lagergren equation, is based on interfacial kinetics. It is provided in Equation (9) (Lagergren 1898):

\[
\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{9}
\]

The pseudo-second-order model describes sorption occurring where one sorbate can interact with more than one sorption site. The linear form of the model is given as Equation (10) (Ho & McKay 1999; Ho 2006):

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}
\]

### Sorption thermodynamics

In the sorption system, thermodynamics parameters \( \Delta G^o \), \( \Delta H^o \), and \( \Delta S^o \) will help define the nature of the removal of MO and Cu(II) using PANI-coated kapok. The parameters

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**Table 2** | Isotherm parameters derived from for the sorption of MO and Cu(II) onto the PANI-coated kapok fibers

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Parameters</th>
<th>Adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Methyl orange</td>
</tr>
<tr>
<td>Langmuir</td>
<td>( q_0 ) (mg/g)</td>
<td>75.76</td>
</tr>
<tr>
<td></td>
<td>( K_L ) (mL/mg)</td>
<td>0.087</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.959</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( K_F ) (mg/g)</td>
<td>21.83</td>
</tr>
<tr>
<td></td>
<td>( N )</td>
<td>4.15</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.910</td>
</tr>
<tr>
<td>D-R</td>
<td>( q_{D-R} ) (mg/g)</td>
<td>60.70</td>
</tr>
<tr>
<td></td>
<td>( E ) (kJ/mol)</td>
<td>1,210.02</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.699</td>
</tr>
</tbody>
</table>
Figure 4 | Plot of experimental data points against the theoretical isotherm curves generated by the Langmuir, Freundlich and D-R models for (a) MO and (b) Cu(II) sorption and kinetic plots using (c) pseudo-first-order and (d) pseudo-second-order equation for the removal of MO and Cu(II) onto PANI-coated kapok.
where $k_2$ is the pseudo-second-order rate constant ($g/mg\cdot min$).

Table 4 shows the kinetic parameters for sorption of MO and Cu(II) onto the PANI-coated kapok. It was observed that the values of $R^2$ for MO and Cu(II) sorption using the pseudo-second-order model are 0.990 and 0.999, respectively. These $R^2$ values indicate that the pseudo-second-order model best fits the experimental data derived from removal of MO and Cu(II) using PANI-coated kapok. Furthermore, the theoretical values of $q_e$ generated by the pseudo-second-order model for MO and Cu(II) are closer to the experimental values. This is further validated by Figure 4(d), where the experimental data points are in good agreement with the theoretical line generated by the pseudo-second-order equation. The said fitness to the pseudo-second-order model implies that the rate determining step for the sorption of MO and Cu(II) is chemisorption. The kinetic rate constant derived from the pseudo-second-order model for Cu(II) has a greater value than MO due to the smaller hydrated ionic radius of Cu(II) where it can diffuse faster and results in better sorption capacity.

Table 5 presents the sorption capacity of other sorbents derived from previous studies that were utilized in the removal of MO and Cu(II). When compared to other sorbents, the sorption capacity of the PANI-coated kapok is satisfactory when compared to sorbents of previous works. This indicates a strong potential for the application of PANI-coated kapok in the removal of MO and Cu(II) from wastewater effluents.

**Sorption mechanism of MO and Cu(II)**

The nitrogen atom of the iminium/imine group, located beside the quinoid ring is potentially reactive, thus it is possible binding sites of various substances. The said nitrogen atom has attached hydrogen atom when PANI is protonated (Figure 5(a)) and has no attached hydrogen atom when

### Table 3  Thermodynamic parameters for the sorption of MO and Cu(II) onto the PANI-coated kapok

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Temperature (K)</th>
<th>$\Delta G$ (kJ/mol)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (kJ/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>298</td>
<td>$-10.11$</td>
<td>$8.96$</td>
<td>$0.064$</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>$-11.54$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>$-13.01$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(II)</td>
<td>298</td>
<td>$-11.32$</td>
<td>$1.32$</td>
<td>$0.042$</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>$-12.37$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>$-13.23$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 4  Estimated kinetic parameters for sorption of MO and Cu(II) onto the PANI-coated kapok

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>$q_{exp}$</th>
<th>$q_e$</th>
<th>$k_1$</th>
<th>$R^2$</th>
<th>$q_e$</th>
<th>$k_2$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>28.43</td>
<td>17.35</td>
<td>0.0074</td>
<td>0.8341</td>
<td>29.37</td>
<td>0.0005</td>
<td>0.9900</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>88.53</td>
<td>11.89</td>
<td>0.0024</td>
<td>0.7537</td>
<td>86.74</td>
<td>0.0011</td>
<td>0.9990</td>
</tr>
</tbody>
</table>

Where $k_1$ is the pseudo-first-order rate constant (min$^{-1}$).

### Table 5  Methyl orange and Cu(II) sorption capacities of different sorbents

<table>
<thead>
<tr>
<th>Sorbate</th>
<th>Sorbent</th>
<th>Sorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>PANI-coated kapok fiber</td>
<td>75.76</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>Polycrylonitrile-coated kapok fiber</td>
<td>34.72</td>
<td>Agcaoili et al. (2017)</td>
</tr>
<tr>
<td></td>
<td>Surfactant-modified silkworm exuviae</td>
<td>87.03</td>
<td>Chen et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>Graphene oxide</td>
<td>16.83</td>
<td>Robati et al. (2016)</td>
</tr>
<tr>
<td></td>
<td>Goethite</td>
<td>55.00</td>
<td>Munagapati et al. (2017)</td>
</tr>
<tr>
<td></td>
<td>Chitosan beads</td>
<td>73.00</td>
<td>Munagapati et al. (2017)</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>PANI-coated kapok fiber</td>
<td>81.04</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>Polycrylonitrile-coated kapok fiber</td>
<td>90.09</td>
<td>Agcaoili et al. (2017)</td>
</tr>
<tr>
<td></td>
<td>Chemically-modified orange peel</td>
<td>72.73</td>
<td>Feng et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>Peanut hull</td>
<td>21.25</td>
<td>Zhu et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>Tartaric acid-modified rice husk</td>
<td>29.00</td>
<td>Wong et al. (2007)</td>
</tr>
</tbody>
</table>
deprotonated (Figure 5(b)). The attached hydrogen atom of the emeraldine salt is loosely bound, where various substances can potentially replace the bound hydrogen atom and bind with the reactive nitrogen atom.

It is assumed that MO anions established bonds with the nitrogen atom of the iminium group of PANI-coated kapok. Their corresponding charges, the negative charge for MO and positive charge for the nitrogen atoms of the PANI-coated kapok, formed electrostatic attraction as bonds that led to their reaction. On the other hand, a covalent bond is formed between Cu(II) and nitrogen atom of the iminium group, which has two lone pair of electrons that could lead to formation of amide copper complexes.

The values of pseudo-second-order rate constant ($k_2$) for MO and Cu(II) ions using the PANI-coated kapok fibers are smaller when compared to the rate constants of previous studies (Feng et al. 2009; Zhu et al. 2009; Chen et al. 2011; Agcaoili et al. 2017). The low values could be attributed to the slow reactions between contaminants and nitrogen atoms due to the displacement of the attached hydrogen atom before the reaction can proceed.

CONCLUSION

Kapok fibers were coated with PANI molecules using an oxidative-type in-situ technique. Infrared spectrum shows vibrational modes associated with the presence of PANI molecules distributed onto the surface of kapok. After the coating process, the water contact angle of the fibers dropped from 120° (highly hydrophobic) to 0° (hydrophilic). Results show that the tubular structure of the kapok fibers was retained after the coating process. In the present study, the capacities of PANI-coated fibers to adsorb MO and Cu(II) were determined to be 75.76 and 81.04 mg/g using the Langmuir isotherm model. Based from the thermodynamic studies, both MO and Cu(II) sorption were evaluated to be spontaneous, feasible and endothermic. Meanwhile, the kinetic data were determined to best fit the pseudo-second-order model, implying that chemisorption is the rate-determining step for the removal of MO and Cu(II) using PANI-coated kapok.

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CONFLICT OF INTEREST

The authors declare that they do not have any conflict of interest.

REFERENCES


Chung, B. Y., Cho, J. Y., Lee, M. H., Wi, S. G., Kim, J. H. & Kim, J. S. 2008 Adsorption of heavy metal ions onto chemically...


Li, D., Yang, Y., Li, C. & Liu, Y. 2017 A mechanistic study on decontamination of methyl orange dyes from aqueous phase by mesoporous pulp waste and polyaniline. Environmental Research 154, 139–144.


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