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Research Article

Adsorption Kinetic Study of Iron Metal Ions in the Batik Cual Waste onto Freshwater Crab (Parathelphusa convexa) Shell Chitosan

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ABSTRACT

Chitosan from freshwater crab (Parathelphusa convexa) shell has been successfully extracted and its kinetic adsorption models for iron (Fe) metal ions in the batik cual waste solution (BCWs) were studied. Freshwater crab chitosan (FwC-Chi) was extracted via demineralization, deproteinization, decolorization, and deacetylation steps. The deacetylation degree value of FwC-Chi was 97.92% determined through FTIR spectra using the baseline method. In this study, iron metal ions distributed in the BCWs homogeneously with the concentration of iron (Fe) was 0.43 mg/L determined by atomic absorption spectroscopy (AAS). The performance of FwC-Chi adsorption on iron in the BCWs with the ratio of 1:100 (w/v) for various contact times of 30, 60, 90, 120, 150, 180, 210, and 240 minutes respectively while stirring homogeneously at room temperature. The result showed that the adsorption kinetic models for iron metal ion in the BCWs follows Behnajady-Modirshahla-Ghanbery (BMG) and pseudo-second-order kinetic model. Based on this model we found that the decrease of iron concentration is indicated by the decolorization of the waste color. It's clear that there is a relationship between the waste color with the concentration of iron metal in the BCWs. The coefficient of decolorization decay, rate of decolorization and adsorption rate coefficient was 1,366 g-1, 16,053 g min^{-1}, and 0,043 g mg^{-1} min^{-1} respectively achieved based on this model.

Introduction

Iron (Fe) metal ions are one of the heavy metals contained in the batik cual waste solution (BCWs) because of the high levels of residual dyes contained in the waste solution.[1] The presence of iron metal ions has potency as a pollutant in the environment and it can increase the risk of chemical substances stored in various aquatic biota especially aquatic commodities as a source of human food.[2] The aquatic commodity products that have been contaminated by heavy metals are very dangerous for human consumption because it is toxic in the long term so that its required removal of iron metals ion treatment from environment.[3-5] Several methods have been used to remove the dyes associated with heavy metals content from batik waste solution such as: electrocoagulation, advanced oxidation processes (AOPs), and adsorption.[6-8] Adsorption is one of removal of heavy metals ion treatment are widely applied because its low cost, high efficiency and environmentally friendly.[9]

Parathelphusa convexa is one of freshwater crab that can be found in aquatic and terrestrial habitat. These crabs are often found in rice fields and make holes in these areas as their hideouts. The existence of these holes causes leaks in rice field irrigation channels so that it decreases effectiveness and the presence of these crabs is often considered a pest by farmers. The high reproductive rate and lack of natural predators of these crabs cause the crab population increase rapidly especially during the rainy season so it is possible that plenty of freshwater crabs exist.[10]

Although these population has not yet been estimated and commercially evaluated in fact, freshwater crabs are an important source of chitin as chitosan precursors like the other crustaceans.[11]

Chitosan has high adsorption ability and environmentally friendly because its non-toxicity and biodegradable.[12] The extraction of chitosan generally consists of three main steps: demineralization, deproteinization, and deacetylation.[12,13] Modifications of chitosan with the optimizing parameters in the extraction process and additional specific treatments are needed to get the desired chitosan performance. Chitosan adsorption kinetic models describe quantitatively the adsorption mechanism. The kinetic models, such as pseudo-first order, pseudo-second order, and BMG models, are based on the determination coefficient (R^2).[7] This model is also able to estimate the rate of the iron metal ions as adsorbate moves from the waste solution to the FwC-Chi as adsorbent.

Materials and methods

Extraction of FwC-Chi

Freshwater crabs (Parathelphusa convexa) known as Yuyu crabs are found in the rice fields habitat, were used. The extraction of FwC-Chi follows taking the crab shells after boiling for 15 min. The shells were dried under sunlight and were ground using a electric blender and sieved with 200 mesh sieve. The powder of crab shells was demineralized with analytical HCl 1.5 M and stirred for 1 hour at room temperature with a solid/solvent ratio of 1:12 (w/v), then rinsed with distilled water until neutral and dried in an oven at 85^{o}C overnight. The deproteination of demineralized crab shell powder was performed with analytical NaOH 2 M and stirred for 1 hour at room temperature with a solid/solvent ratio of 1:6 (w/v), then rinsed with distilled water until neutral and dried in an oven at 85^{o}C overnight to obtain chitin. The chitin powder was bleached using analytical NaClO 5% with a solid/solvent ratio of 1:10 (w/v) stirred for 1 hour at room temperature, then rinsed until neutral and dried in an oven at 85^{o}C overnight to obtain fine chitin. The deacetylation of chitin was achieved by treatment of fine chitin under conditions of room temperature with 60% analytical NaOH and stirred for 1 hour and a solid/solvent ratio of 1:10 (w/v), then rinsed until neutral and dried in an oven at 85^{o}C overnight to obtain FwC-Chi. The deacetylation degree (DD) of FwC-Chi is calculated using the baseline method based on Fourier transform infrared (FTIR) spectra were recorded using Thermo Fisher Scientific Nicolet 8700 spectrophotometer according to Equation (1) below:

$$DD = (100 - \left(\left(\frac{A_{1655}}{A_{3450}}\right) x \frac{100}{1.33}\right)\% \qquad (1)$$

Where A_{1655} and A_{3450} are the absorbances of the amide band and hydroxyl band respectively. A factor of 1.33 showed the ratio value of A_{1655}/A_{3450} for chitin deacetylation completely.

The iron adsorption method

The batik cual waste (BCWs) are collected from batik cual home industry around Pangkalpinang city. Preparation of the BCWs aimed to distributing the iron metal ions homogeneously was performed by stirring for 1 hour at room temperature. The concentration of iron (Fe) metal ions in the BCWs after preparation was 0.43 mg/L determined by atomic absorption spectroscopy (AAS) Shimadzu AA 6300. The adsorption process started by making BCWs standard 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, and 0% with distilled water where BCWs standard 100% are prepared BCWs and BCWs standard 0% are distilled water. The BCWs standard was tested using UV-Vis Shimadzu 1800 spectrophotometer with wavelength measured from 200 - 900 nm respectively. The relationship of iron metal ions concentration in the BCWs standard with maximum absorbance value obtained based on UV-Vis data expressed in linear equation from the graph of iron metal ions concentration Vs maximum absorbance value (conversion equation) where it used to convert the maximum absorbance value of BCWs after treatment to iron metal ions concentration. The performance of FwC-Chi adsorption on iron metal ions in the BCWs with ratio of 1:100 (w/v) while stirring for 5 min and then left in variation contact time: 30, 60, 90, 120, 150, 180, 210, and 240 min at room temperature. The iron metal ions content after treatment was calculated by conversion equation based on the UV-Vis data of BCWs after adsorption. The analysis of the adsorption kinetic models of iron metal ions in the BCWs onto the FwC-Chi was carried out using pseudo-first, second-order and BMG kinetic models using Wolfram Mathematica 11.3 software are based on the determination coefficient (R^2). The analysis of the pseudo-first, second-order and BMG kinetic models of iron metal ions adsorption onto FwC-Chi are based on the Equation 2, 3, and 4 respectively follows:

$$C = C_0 e^{-kt} \tag{2}$$

$$C = \frac{C_0}{1+kC_0 t} \tag{3}$$

$$C = C_0 \left(1 - \frac{t}{m+bt}\right) \tag{4}$$

Where C is the concentration of iron metal ions of solution after treatment (mg/L), C_o is the initial concentration of iron metal ions in the BCWs after preparation (mg/L), k is is the coefficient of FwC-Chi adsorption rate (g mg^{-1} min^{-1}), t is the contact time (min), b is the coefficient of decolorization decay (g^{-1}) and m is the rate of decolorization (g min^{-1}).

Results and discussion

FTIR analysis

The characteristics of FwC-Chi described based on FTIR spectra are marked with red dots wavenumber are shown in Figure 1.

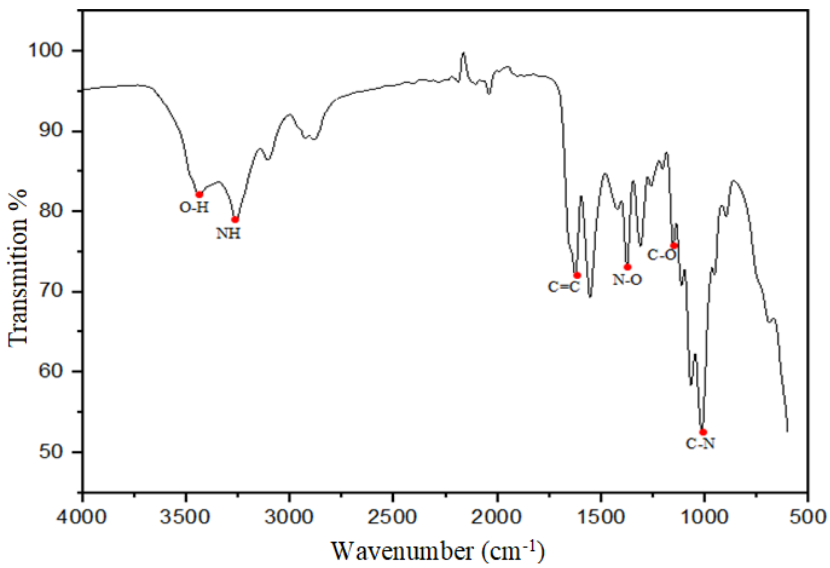


Figure 1. The FwC-Chi FTIR spectra

The red dot shows that in the FwC-Chi compound there is an O-H, N-H, C=C, N-O, C-O and C-N group in the absorption band 3435.40, 3258.23, 1622.78, 1374.95, 1152.42, and 1014.58 cm^{-1} respectively. The presence of each functional group indicates that FwC-Chi was successfully extracted from freshwater crabs (*Parathelphusa convexa*) shells confirmed by Table 1. The broad band at about 3435.40 cm^{-1} and the bands nearly disappeared at 3258.23 cm^{-1} indicate stretching of N-H after deacetylation. It is confirmed by the reduction of bands at 1622.78 cm^{-1} and 1374.95 cm^{-1} assigned to the stretching of C=O in amide bond and CO-NH bending vibration respectively indicating that the deacetylation process was successfully carried out.

Table 1. The functional group of chitosan standard [14]

The functional group	Wavenumber (cm^{-1})
O-H	3650-3400
N-H	3500-3100
C=C	2250-2100
N-O	1550-1350
C-O	1300-1000
C-N	1350-1000

UV-Vis spectra analysis

The graph of absorbance value (A) Vs wavelength (λ) from BCWs standard is relatively have same pattern at 400 – 700 nm for BCWs standard 10 - 100% with different absorbance values shown in Figure 2. It indicated that color degradation is more dominant than color change in the making of BCWs standart. It confirms that color degradation occurs by a gradation of dark color to no color (clear one) are shown in Figure 3a. The curve of BCWs standard 0% showed a linear pattern is so different ones (no absorption happens) it may due to the UV-Vis totally transmitted. In addition, an increase in color degradation means a change from dark to clear one causes a decrease in UV-Vis absorbance.

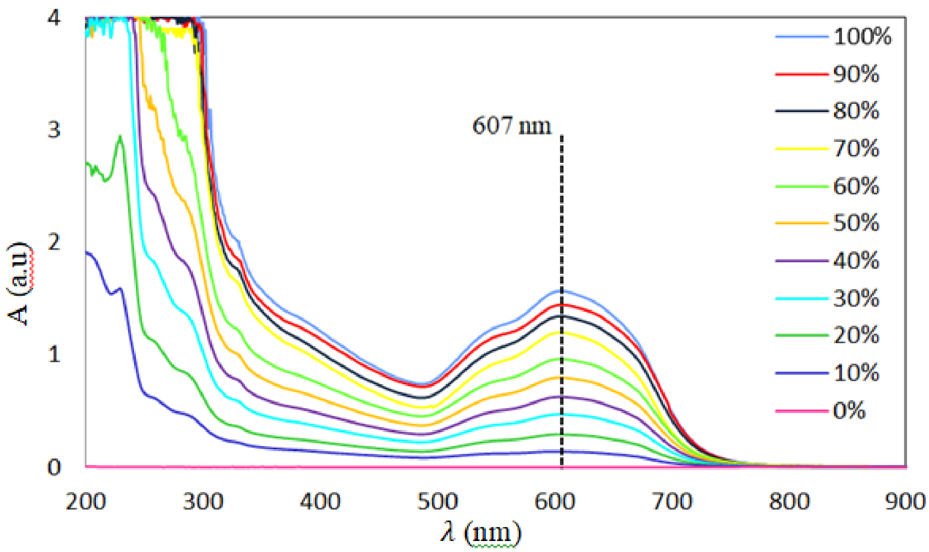
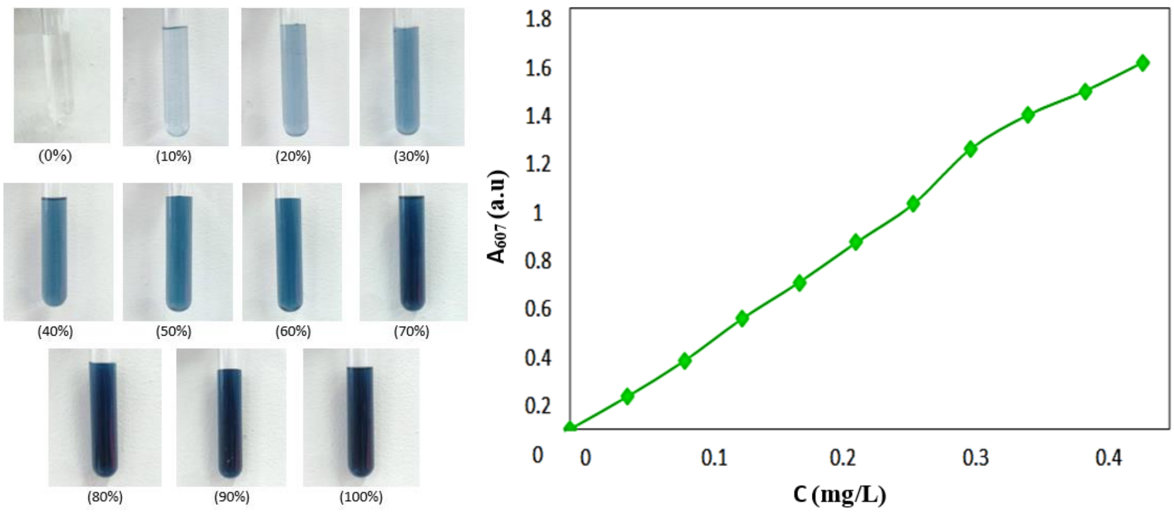


Figure 2. UV-Vis spectra of BCWs standard

The maximum absorbance of UV-Vis (peak of the curve) is found at 607 nm as a reference to make the graph of iron metal ions concentration (C) Vs maximum absorbance value (A_{607}) lead to the conversion equation are shown in Figure 3b.



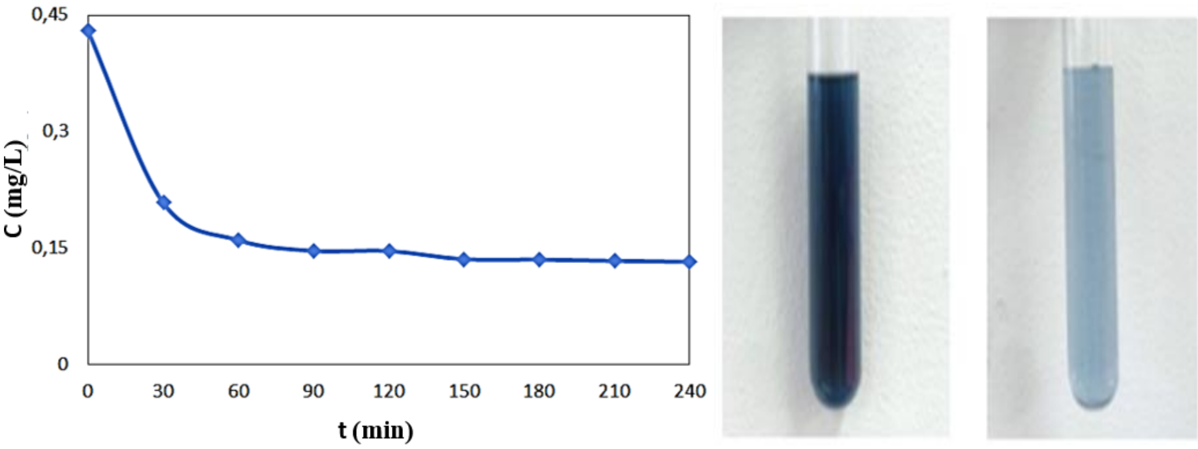
(a) **(b)**

Figure 3. (a) The BCWs standard UV-Vis and **(b)** the C Vs A_{607} graph of BCWs standard

The conversion equation based on C Vs A_{607} graph of BCWs standard represented by Equation 5 below:

$$A_{607} = 3{,}8068C - 0{,}0145 \quad (5)$$

Based on Equation 5, its linear equation which has a positive gradient value and shows that the increase of the C value followed the increase of the A_{607} value. It can be observed in Figure 4, that the saturation condition of iron adsorption occurs at a contact time of 150 min which is characterized by an increase in the concentration of the adsorbed iron metal which is relatively insignificant at the next contact time but the contact time of 60 min is suggested to get the effective condition in this case.



(a) **(b)** **(c)**

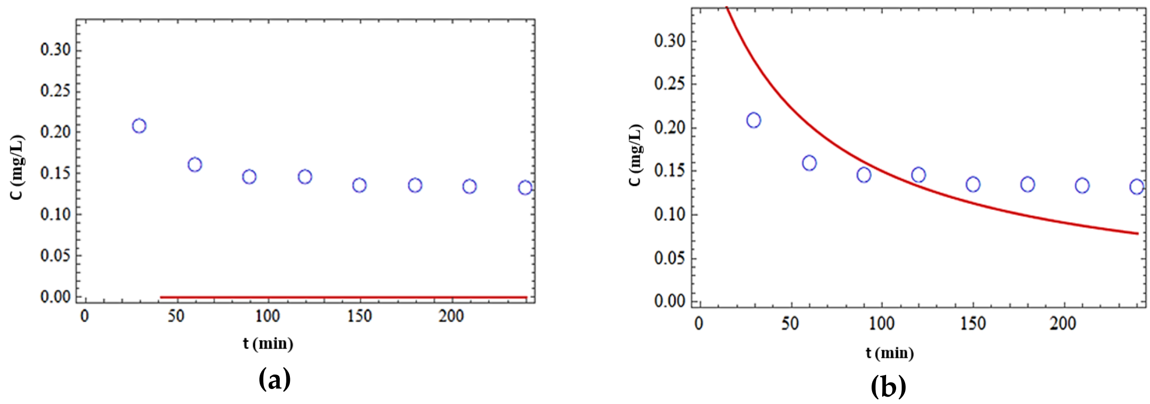
Figure 4. (a) The C value of iron metal ions of solution after treatment at various contact times, **(b)** The BCWs standard, and **(c)** The BCWs after treatment left at 60 min.

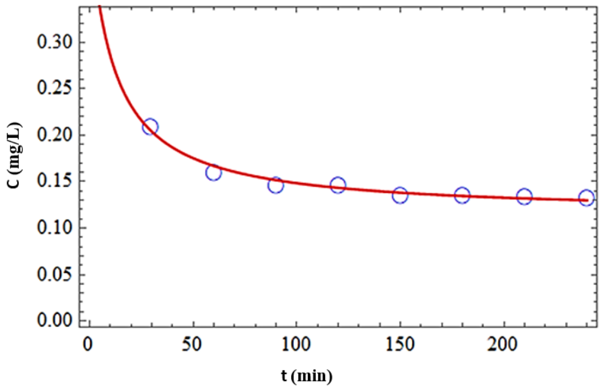
The concentration of iron metal ions of solution after treatment decreased with increasing contact time. It confirms that color degradation occurs by a gradation of the BCWs standard color before and after adsorption are shown in Figure 4b and 4c. Generally, the effectiveness of chitosan adsorb heavy metal ions in the same conditions is influenced by the chitosan degree of deacetylation (chitosan DD). In previous studies explained that the chitosan DD affects the adsorption ability of chitosan as an adsorbent.[12] If the chitosan DD is greater, the adsorption ability of chitosan will be better. Based on the value of the FwC-Chi DD was 97.92%, it becomes a support for its adsorption ability which can optimally decrease iron metal ions and be associated with color degradation in the BCWs. The quantitative constant of adsorption and the determination coefficient of each models are shown in Table 2.

Table 2 . The adsorption kinetic model of iron metals in the BCWs onto FwC-Chi

The adsorption kinetics model	The quantitative constant of adsorption	The determination coefficient (R^2)
The pseudo-first-order	k = 0.9 g mg^{-1} min^{-1}	0.438
The pseudo-second-order	k = 0.043 g mg^{-1} min^{-1}	0.958
The BMG's model	m = 16.053 g min^{-1} b = 1.366 g^{-1}	0.999

The determination coefficient value of the adsorption kinetics equation in pseudo-first is smallest one than other models in Table 2. This indicates that the pseudo-first-order model cannot describe representatively the kinetic mechanism of iron metal adsorption in the BCWs onto FwC-Chi. The value of the adsorption rate obtained is proportional to the coefficient of decolorization decay and rate of decolorization. This indicates that the greater of the adsorption rate value of FwC-Chi, the adsorption of iron metal ions in the BCWs process will run faster and lead to the color degradation process in the BCWs increase.





(c)

Figure 5. The adsorption kinetic models of iron metal ions in the BCWs onto FwC-Chi: **(a)** the first-order, **(b)** the second-order, and (c) the BMG's model.

Conclusion

The adsorption kinetic models for iron metal ion in the BCWs onto FwC-Chi follows Behnajady-Modirshahla-Ghanbery (BMG) and pseudo-second-order kinetic model. The coefficient of decolorization decay, rate of decolorization and adsorption rate coefficient was 1,366 g^{-1}, 16,053 g min^{-1}, and 0,043 g mg^{-1} min^{-1} respectively achieved based on this model. The decrease of iron concentration is indicated by the decolorization of the waste color.

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Conflicts of Interest

The authors listed above have no conflicts of interest.

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