Adsorption of methylene blue and ferrous metal solution by using coconut shell charcoal

Natkrita Prasoetsopha[a], Intira Soonsook[b], Anussara Panyayaw[b], Paphawarin Nanon[b], Witawat Singsang[c], Ing-orn Sittitanadol[b, *]

[a] Department of Materials Engineering, Faculty of Engineering and Technology, Rajamangala University of Technology Isan, Nakhon Ratchasima, 30000 Thailand.
[b] Department of Metallurgical Engineering, Faculty of Engineering, Rajamangala University of Technology Isan, Khon Kaen Campus, Khon Kaen, 40000 Thailand.
[c] Department of Aircraft Part Manufacturing Technology, Faculty of Industrial Technology, Rambhai Barni Rajabhat University, Chanthaburi, 22000 Thailand.

***Corresponding Author:** ingorn.si@rmuti.ac.th
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Abstract

This research was developed based on the problem of waste from the coconut export industry and the current trend of water pollution. This research aims to study methylene blue adsorption by using coconut shell charcoal prepared from clay kilns. The study of adsorption isotherms in batch experiments showed that the coconut shell charcoal was fitted well with Langmuir adsorption isotherms with a capacity of 36.49 mg g^{-1} for particle size in the range of 53 – 74 μm. Through the determination of the surface area of methylene blue adsorption, coconut shell charcoal in the range of 53 – 74 micrometers had the highest surface area of 65.95 m^2 g^{-1}. Coconut shell charcoal was used to study the adsorption of ferrous ion from aqueous solution at the initial concentration of 15 mg l^{-1}. It was found that 0.25 g of coconut shell charcoal had the highest absorption capacity of 17.29% of the ferrous ion.

Keywords: Adsorption; coconut shell charcoal; Methylene blue; Ferrous ion; Heavy metal

Introduction

Nowadays, a large amount of hazardous and toxic chemicals such as dyes, pesticides, heavy metals, industrial waste, and various chemicals are released into natural water sources. This is a major problem for the environment due to their toxic effect on humans and aquatic organisms, both directly and indirectly [1]. There are several methods to treat wastewater such as filtration, adsorption, ozonation, photocatalyst, chlorine treatment and so on [2 – 4]. One of the most popular methods is the adsorption process, given its simplicity, cost-effectiveness, environmental friendliness, and high wastewater treatment efficiency [5]. Finding simple and effective adsorbents to use in the wastewater treatment process is one way to reduce environmental problems.

Apart from being used as fuel, charcoal has high adsorption properties making it suitable for wastewater treatment. Activated carbon has been frequently used as adsorbent to absorb dyes, heavy metals, and organic and inorganic substances from wastewater [6]. A study on the preparation of activated carbon from empty fruit bunches and mesocarp fibers of oil palm conducted by Baloo L. et al. [7] showed that the prepared activated carbon could be used as adsorbents for wastewater treatment. In the experiments, the prepared activated carbon had a maximum adsorption capacity of methylene blue (MB) of 24 mg g^{-1} and the maximum adsorption capacity of acid orange 10 (MO10) of 18.76 mg g^{-1}.

Yusop M.F.M. et al. [5] studied the preparation of activated carbon from acacia wood as an adsorbent for wastewater treatment. The physicochemical activation process was used to prepare activated carbon from acacia. It was found that the activated carbon from acacia fit well with Langmuir's equation and had an adsorption capacity of 338.29 mg g^{-1}. Similarly, the study of Zakaria R. et al. [8] found that activated carbon prepared from Mangrove pile leftovers chemically activated by phosphoric acid (H_3PO_4) showed a monolayer adsorption behavior according to Langmuir's equation and had the adsorption capacity of 72.20 mg g^{-1}.

However, the preparation of activated carbon is varied and cumbersome. Therefore, adsorbent charcoal prepared from natural waste material is an economical and environmentally friendly technology for the removal of dyes and heavy metals. Coconut is one of the most important economic crops in Thailand. After harvest, farmers dispose of coconut shells through incineration, which causes pollution. As a result, researchers are interested in using coconut shell charcoal as adsorbents to reduce environmental problems directly and indirectly. In this paper, coconut shell charcoal was investigated for the absorption of methylene blue dye and ferrous ion, which represent wastewater pollutants, including the isotherms and surface area of methylene blue adsorption.

Materials and Methods

Preparation and characterization of coconut shell charcoal

The coconut shell was calcined in a kiln originating in folk wisdom and having the same functions as the Elsa stove [9], then grounded into a fine powder and sieved through meshes to obtain a powder with the sizes of 1,190 – 1,680, 149 – 210, and 53 – 74 µm. SEM (FEI, QUANTA 250), FTIR (Perklin Elmer, Frontier), and XRD (Rigagu, SmartLab SE) were used to observe the surface morphology, surface functional groups, and phase composition of the prepared coconut shell charcoal, respectively. Moreover, the specific surface area and total pore volume were examined using nitrogen adsorption Brunaner-Emmett-Teller (BET) analysis (Micrometrics 3Flex, Version 5.02 apparatus).

Adsorption of methylene blue experiment

The adsorption isotherms and surface area were determined by the batch method. Coconut shell charcoal sizes 1,190 – 1,680, 149 – 210, and 53 – 74 µm were used. Adsorption was performed with 0.25 g of coconut shell charcoal added to 150 mL of methylene blue solution (MB, Nice chemical Pvt, Ltd.) with the different initial concentrations of 3, 10, 20, 30, 40, and 50 mg l^{-1} then stirred in the dark for 7 h at equilibrium. The remaining concentration of MB was determined using a UV-visible spectrophotometer (Jasco V530) at wavelength 664 nm [10, 11]. The equilibrium adsorption capacities (Q_e) in mg g^{-1} was calculated using the eq. (1) [11]:

$$Q_e = \left(\frac{C_0 - C_e}{M}\right)V \qquad (1)$$

Where C_0 is the initial concentration in mg l^{-1}, C_e is the equilibrium concentration in mg l^{-1}, V is the liquid phase volume in L, and M is the mass of the adsorbent in mg. The specific surface area of coconut shell charcoal in m^2 g^{-1} was calculated using the following eq. (2) [12, 13]:

$$S_{MB} = \frac{N_g \times a_{MB} \times N \times 10^{-20}}{M} \qquad (2)$$

Where N_g is the number of molecules of MB dye adsorbed at the monolayer of charcoal in mg g^{-1}, a_{MB} is the occupied surface area of one molecule of MB dye (197.20 $Å^2$), N is Avogadro's number (6.02×10^{23} mol^{-1}) and M is the molecular weight of MB dye (373.90 g mol^{-1}).

Adsorption of ferrous ion experiment

Adsorption of ferrous ion from aqueous solution of various sizes of prepared coconut shell charcoal was determined by the batch method. 0.25 g of coconut shell charcoal was added to 150 ml of ferrous ion solution (Ammonium Iron (II) Sulfate Hexahydrate) at an initial concentration of 15 mg L^{-1}, then stirred in the dark for 7 h at equilibrium. The concentration of the residual ferrous ion was measured using a UV-visible spectrometer at wavelength 510 nm [14]. The percentage removal of the ferrous metal was calculated using eq. (3) [10]:

$$\%Removeal = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \qquad (3)$$

Where C_0 is the initial concentration in mg l^{-1} and C_e is the equilibrium concentration in mg l^{-1}.

Table 1 Langmuir and Freundlich parameters for the adsorption of methylene blue onto coconut shell charcoal adsorbent.

Sample (µm)	Langmuir model			Freundlich model		
	b	q_0	R^2	K_f	n^{-1}	R^2
53 – 74	1.45	36.49	0.9809	4.76	0.67	0.9112
149 – 210	0.17	21.29	0.9855	3.34	0.55	0.9579
1,190 – 1,680	0.12	3.89	0.9858	0.72	0.41	0.8809

Results and Discussions

Characterization of coconut shell charcoal powder

Fig. 1 shows an SEM image of the surface morphology of the coconut shell charcoal. The surface was found to be rough and filled with cavities of different sizes. This surface will help to support the increased adsorption capacity because the dye molecules are absorbed into the pores, consistent with the study of Nipa S.T. et al. [15], which discovered that the irregular surface structure and a large number of pores of papaya increase the ability to absorb.

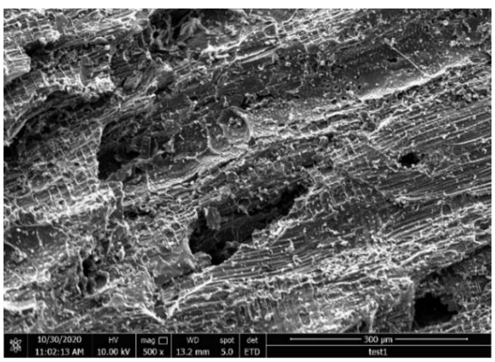

Fig. 1 Surface morphology of the coconut shell charcoal.

Adsorption isotherm

The adsorption isotherms to characterize the adsorption mechanism of methylene blue onto coconut shell charcoal were studied through the Langmuir eq. (4) and Freundlich eq. (5) [18]:

$$\frac{1}{q_e}=\frac{1}{Q_0}+\left(\frac{1}{bQ_0}\right)\left(\frac{1}{C_e}\right) \qquad (4)$$

$$q_e=K_f C_e^{1/n} \qquad (5)$$

Where q_e is the amount of solute adsorbed in mg g^{-1}, C_e is the equilibrium concentration in mg l^{-1}, Q_0 is the monolayer adsorption capacity in mg g^{-1}, b is the constant related to the energy of adsorption in L g^{-1}, K_f and n are Freundlich's constants.

The adsorption of methylene blue onto coconut shell charcoal powder experiment showed that the adsorption occurred early and reached equilibrium after 3 h. As shown in Fig. 3((a), (b)), the adsorption isotherm was better fitted by the Langmuir models than the Freundlich models because the correlation coefficient (R^2) was closer to 1 (Table 1). The Langmuir models signify monolayer physisorption [19] on adsorbents. The coconut shell charcoal size of 53 – 74 µm produced the highest adsorption capacity of 36.49 mg g^{-1}.

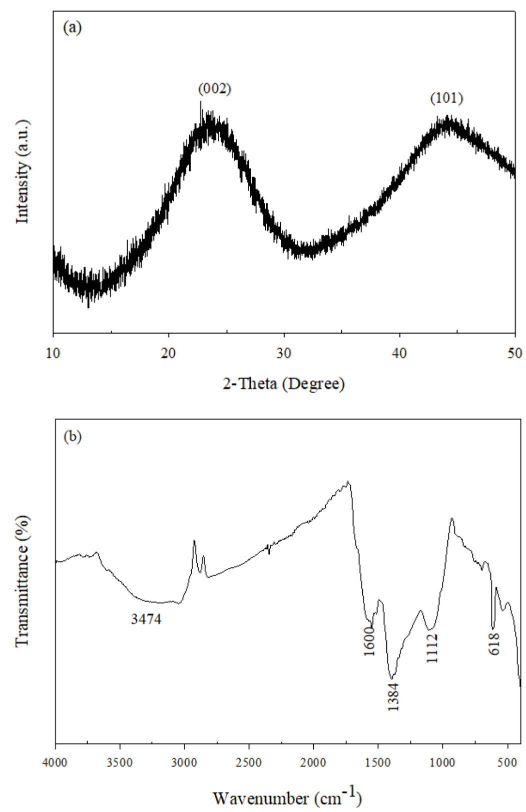

Fig. 2 (a) XRD pattern and (b) FTIR spectra of coconut shell charcoal.

Table 2 The calculated specific surface area, BET specific surface area, and total pore volume of coconut shell charcoal powder.

Sample (µm)	N_g (mg g^{-1})	S_{MB} (m^2 g^{-1})	S_{MB} (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})
53 – 74	20.77	65.95	235.69	0.160
149 – 210	15.76	50.05	188.55	0.123
1,190 – 1,680	2.96	9.80	104.66	0.067

The X-ray diffraction (XRD) pattern of the coconut shell charcoal (Fig. 2(a)) shows the board peaks at 24.1^O and 43.9^O, indicating an amorphous carbon structure corresponding to the (002) and (101) planes of carbon [16]. Fig. 2(b) interprets the FTIR spectra of coconut shell charcoal, which has all the necessary bands to prove that it is charcoal. The C-C stretching is linked to the bands at 430 and 618 cm^{-1}, whereas the C-O vibration is associated with 1112 cm^{-1}. Bands were found at 1384 and 1600 cm^{-1} are confirmed to be the C-H symmetric bending and C-C aromatic skeletal stretching vibrations, respectively. The O-H stretching vibrations are responsible for the bands around 3474 cm^{-1} [16, 17].

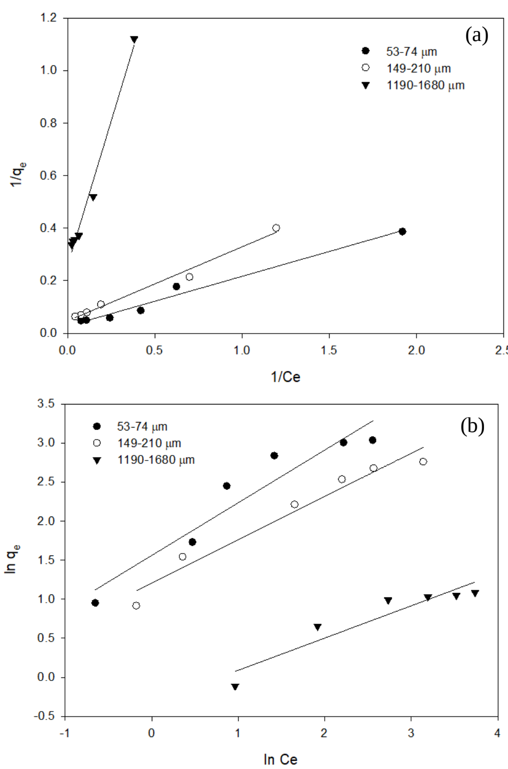

Fig. 3 Plot of adsorption isotherms for the adsorption of methylene blue onto coconut shell charcoal adsorbent; (a) Langmuir model and (b) Freundlich model.

Through determination of specific surface area of coconut shell charcoal powder from methylene blue adsorption capacity, it was found that the coconut shell charcoal with particle size in the range of 53 – 74 µm had the highest specific surface area, followed by sizes 149 – 210 and 1,190 – 1,680 µm, respectively, as shown in Table 2, because small particles have greater surface area than larger particles consistent with the work of Albalasmeh A. et al. [13]. It was also found that larger biochar particles had less surface area than smaller biochar particles.

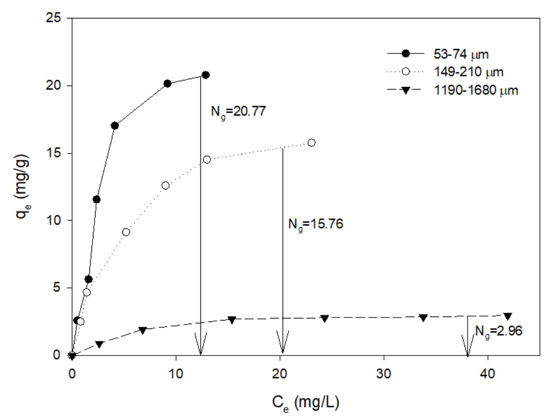

Fig. 4 Adsorption isotherm of methylene blue solution onto coconut shell charcoal adsorbents.

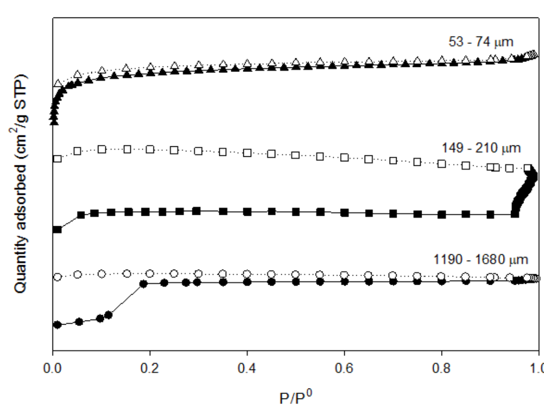

Fig. 5 Nitrogen adsorption-desorption isotherm of coconut shell charcoal.

The nitrogen adsorption–desorption isotherms of all sizes of coconut shell charcoal shown in Fig. 5 show that it is a Type I and Type II isotherm according to the IUPAC classification [5], which means it is a microporous and mesoporous material with a small surface area. Also, Brunauer-Emmett-Teller (BET) analysis showed that as the size of the particles gets smaller, the charcoal gets more porous and has a bigger surface area. And the BET surface area of prepared coconut shell charcoals was consistent with the study of preparation of porous graphene-like material from coconut shell charcoals for supercapacitors by Fahmi F. et al. [20] found that BET surface area of coconut shell charcoals with a size of 125 µm is 189.97 m^2 g^{-1}.

Adsorption of ferrous ion

The adsorption of ferrous ion from aqueous solution onto coconut shell charcoal powder study showed that coconut shell charcoal had the ability to absorb ferrous ion with the coconut shell charcoal size 53 – 74 µm being the most effective. It could absorb 17.29% of ferrous ion, while coconut shell charcoal size 149 – 210 and 1,190 – 1,680 µm could absorb 8.17% and 3.03% of ferrous ion, respectively. The highest absorption capacity of ferrous ion was made by coconut shell charcoal size 53 – 74 µm. This result is similar to the adsorption of the methylene blue solution, thanks to its largest surface area.

Conclusion

The methylene blue absorption of coconut shell charcoal was a monolayer physisorption. The coconut shell charcoal size 53 – 74 µm had the highest adsorption capacity at 36.49 mg g^{-1}. The prepared coconut shell charcoal had surface areas of 65.95, 50.05, and 9.80 m^2 g^{-1} for the coconut shell charcoal sizes of 53 – 74, 149 – 210, and 1,190 – 1,680 µm, respectively. For the adsorption of the ferrous ion from aqueous solution, it was found that coconut shell charcoal size 53 – 74 µm was more effective than other sizes, since it presented the highest adsorption capacity and highest specific surface area. At an initial concentration of 15 mg l^{-1}, 0.25 g of coconut shell charcoal had the highest capacity of ferrous ion adsorption at 17.29%.

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