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Magnetically Modified Corn Cob as a New Low-Cost Biosorbent for Removal of Cu (II) and Zn (II) from Wastewater

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Abstract

Wastewater containing heavy metals can potentially harm the human and living organisms and also damage the environment and ecosystem. Wastewater containing total copper (Cu) and zinc (Zn) over the normal threshold will result in Wilson's disease and digestive health, respectively. One of the most widely used methods to remove heavy metals from wastewater is adsorption. One type of adsorbent that has gained interest among researchers was biomass-based adsorbent or biosorbent. In this work, magnetic modification was used to increase the adsorption capacity of the biosorbent. Therefore, the aim of this study was to determine the effect of magnetic modification of corncobs as biosorbent on the adsorption of Cu(II) and Zn(II) heavy metals from an aqueous solution. Magnetic modification with $FeCl_3.7H_2O$ on corncobs has successfully increased the adsorption capability of Zn(II) and Cu(II) from aqueous solution. The optimum modification ratios for the adsorption of Zn(II) and Cu(II) were 1:2 and 2:1. The adsorption of these both heavy metals took place at temperature of 50°C with the adsorbent doses of 1 g and 1.5 g for Cu(II) and Zn(II), respectively. The highest adsorption percentages for the adsorption of Zn(II) and Cu(II) were 89.3% and 89.2%, respectively. Whereas, the maximum adsorption capacities of Cu(II) and Zn(II) were 75.76 mg/g and 63.93 mg/g, respectively. The adsorption mechanism of Zn(II) and Cu(II) has followed the Freundlich isothermal adsorption model.

INTRODUCTION

Wastewater containing heavy metals which comes from the mining sector and industrial processes can potentially harm the human and living organisms and damage the environment and ecosystem. Copper (Cu) content in wastewater above the normal threshold can cause wilson disease (hepatolenticular degeneration), which is a genetic disorder caused by accumulation of copper in various vital organs such as liver, brain and cornea if consumed by humans. This disease will cause malfunction of the central nervous system and even death (Singh et al., 2018). On the other hand, wastewater that contains zinc (Zn) over the normal threshold will have an impact on digestive health if consumed (World Health Organization & International Program on Chemical Safety, 1993).

Heavy metal contamination in water can be controlled using precipitation methods, membranes (Soo et al., 2020), chelating resin (Ulloa et al., 2020), electrocoagulation (Tegladza et al., 2021), filtration (Manna et al., 2020), flocculation (Y. Sun, 2020), coagulation (Charerntanyarak, 2009), ion exchange (Tavakoli et al., 2017) and adsorption. So far, the most frequently used heavy metal waste treatment process is adsorption because the manufacturing process is relatively easy and the

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availability of materials that can be used to adsorb heavy metal from wastewater. The adsorption of heavy metal can utilize microorganisms as adsorbent, such as: microalgae, bacteria, and fungi (Wang & Chen, 2009). It can also utilize biomass or biomass waste, such as watermelon peel, wheat stalks (J. Sun et al., 2014), etc. Biomass-based adsorbent has several advantages, such as environmentally friendly, low cost, and enabling economic added value of the biomass waste (Lakshmipathy & Sarada, 2013). This biomass waste has organic chemical bonds which are naturally able to bind positive ions (Buasri et al., 2012).

Corn cobs is considered as one of agricultural waste which has been underutilized. This corncob contains 36% hemicellulose, 40% cellulose, and 16% lignin. In recent years, to increase the adsorption capacity of biomass-based adsorbents, several researchers have developed magnetic modifications by utilizing magnetic modifiers such as Fe_2O_3 (Subana et al., 2020), Fe_3O_4 nanoparticles (Namvar-Mahboub et al., 2020) $FeCl_3.7H_2O$ (Zhang et al., 2020) and $FeSO_4.3H_2O$ (Pan et al., 2014). Therefore, objectives of this study was to study the effect of magnetic modification on the corn cobs as biosorbent to adsorb Cu(II) and Zn(II) from aqueous solution.

MATERIALS AND METHODS

Tools and Materials

The main raw material used in this work was corncobs which obtained from corn farmers in the Kaliurang area, Yogyakarta city. Whereas, methanol (Merck), $CuSO_4$, $ZnSO_4$, and $FeCl_3.7H_2O$ were obtained from local chemical store. The tools used in this work were grinder, digital balance, Whatmann's ash free filter paper, laboratorium oven, magnetic stirrer, thermometer, and Pyrex glass wares. Whereas, for the characterization, Atomic Absorption spectroscopy (AAS) (Agilent type 280 FS), Fourier transform infrared spectroscopy (FTIR) (Thermo Nicolet Avatar 360) were used.

Preparation of Biosorbent

To prepare the biosorbent, firstly, the corncobs were washed and then dried in an oven at 60 °C until constant mass. The dried corn cobs were grinded into powder, and then sieved using a 40 mesh sieve. The screened corn cobs powder was then stored in a closed container for further process.

Magnetic Modification of Biosorbent

The prepared corncobs powder was modified magnetically by using $FeCl_3.7H_2O$ as magnetic modifier. First, corn cobs powder was weighed using a digital balance then added with a solution of methanol-$FeCl_3.7H_2O$ with variations in the mass ratio of corn cobs powder and magnetic modifier of 1:1, 1:2, 1:4, 1:8, 2:1 and 4:1 (w/w). The mixture was then stirred at a speed of 900 ppm. Afterward, the mixture was activated by heat treatment using a furnace at 95°C for 12 hours. Magnetically modified corncob biosorbent was then stored in an airtight container for further uses, e.g. FT-IR characterization, adsorption tests.

Batch Adsorption Process

A set of adsorption experiments were conducted to study the performance of the biosorbent to remove Cu(II) and Zn(II) from aqueous solution. Several biosorbents with varied weights of 1, 1.5, 2, 2.5 and 3 g were mixed with 25 mL of aqueous solution of Zn(II) and Cu(II) at different concentrations (i.e. 100, 200, 300, 400, 500 ppm) which represent the synthetic wastewater. for 30 minutes at varied temperatures (i.e. 30°C, 40°C, 50°C and 60°C). The concentrations of Cu(II) and Pb(II) prior and after adsorption tests were determined using AAS. The experimental design of this current research is shown in Table 1.

Table 1. Experimental designs.

Modifier ratio (native corn cob:$FeCl_3$ g/g)	Adsorbents dose (g)	Initial concentration of synthetic waste (ppm)	Adsorption temperature (°C)
1:1	1	100	30
1:2	1.5	200	40
1:4	2	300	50
1:8	2.5	400	60
2:1	3	500	
4:1			

RESULTS AND DISCUSSION

Effect of Modification on The Chemical Bond of The Biosorbent

The chemical bonds in the biosorbent were characterized using FT-IR. Figure 1 and Figure 2 show the FT-IR spectra of the corncobs prior and after magnetic modification at wavelength range of 400-1200 cm^{-1} and 2,000 - 4,000 cm^{-1}, respectively. The presence of peaks in the FTIR spectra indicates that there were chemical bonds in the wavelength range. Figure 1 shows that there was a peak at wavelength of 580 - 592 cm^{-1} that represent Fe-O bond (Qiao et al., 2018). It can be concluded that the magnetic modification process was successful. Additionally, both biosorbents (i.e. before and after modification) displayed peaks in the 3,300 cm^{-1} wavelength range which indicates the presence of a hydroxyl (-OH) bond which is known to be able to bind cations (Sajayan et al., 2017).

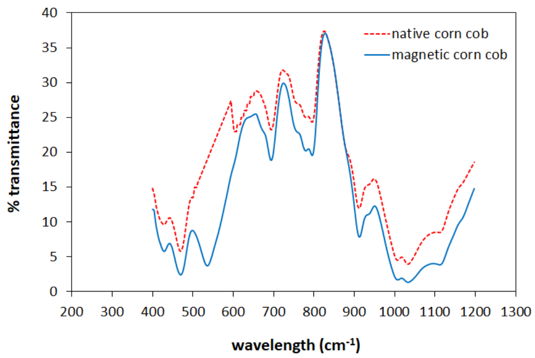

Figure 1. FT-IR spectra of native and magnetic corncobs in the wavelength range of 400-1200 cm^{-1}.

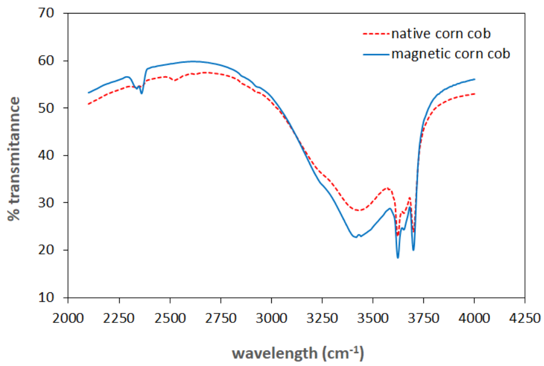

Figure 2. FT-IR spectrum of native and magnetic corncobs in the wavelength range of 2,000 - 4,000 cm^{-1}.

Effect of modification on the adsorption process

The effect of the amount of $FeCl_3.7H_2O$ during the magnetic modification process on the removal percentage of Cu(II) and Zn(II) is presented in Figure 3. The hydroxyl bonds present in corn cobs can naturally bind cations in the synthetic waste (Velmurugan et al., 2015). As shown in Figure 3, the performance of pure/native corn cobs in adsorbing Cu(II) and Zn(II) were quite good, in which the removal percentage were at 66.1% and 73.6% for Cu(II) and Zn(II), respectively. Additionally, as seen in the figure, the removal percentages of Cu(II) and Zn(II) for all of the modified biosorbents samples were higher than the native biosorbent (i.e. corncobs). The optimum Zn(II) adsorption process occurred at a modification ratio of 1:2, while the Cu(II) adsorption process occurred at a 2:1 modification ratio with the removal percentages of 86% and 81.3%, respectively. This improvement of adsorption performance of biosorbent was due to the magnetic modification of the corn cobs using $FeCl_3.7H_2O$. The Fe ion which was impregnated on the adsorbent had a significant impact on the increase of number of cations that can be adsorbed by the adsorbent (Rocher et al., 2008).

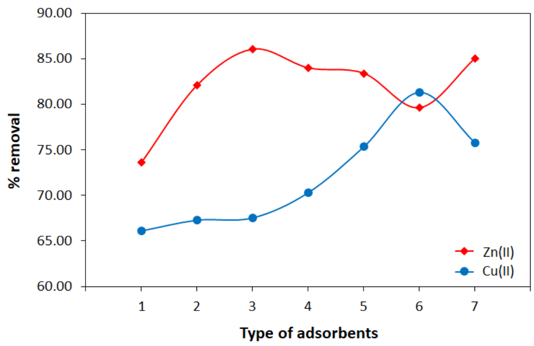

Figure 3. Effect of magnetic modification on the removal percentage of Cu(II) and Zn(II) wastes (i.e. 1: native corncob adsorbent, 2-7: magnetically modified cob adsorbent with modification ratio 1: 1, 1: 2, 1: 4, 1: 8, 2: 1 and 4: 1) at 30°C with initial concentration of 100 ppm synthetic waste.

Effect of Adsorbent Dose on Adsorption Efficiency

The effect of adsorbent doses on the adsorption efficiency of Cu(II) and Zn(II) is shown in Figure 4. One of the factors that can affect the adsorption process of heavy metal waste is the adsorbent dose. It is because the increasing dose of adsorbent will be linear with an increase in the strength of the inter molecular bonds in the adsorbent (Sari et al., 2017) until the optimum condition. As seen in the figure, the optimum dose for the adsorption of Cu(II) and Zn(II) by this magnetic modified biosorbent of corncobs was at a dose of 1 gram for Zn with an absorption efficiency of 86% and a dose of 1.5 grams for Cu with an absorption efficiency of 87.9%.

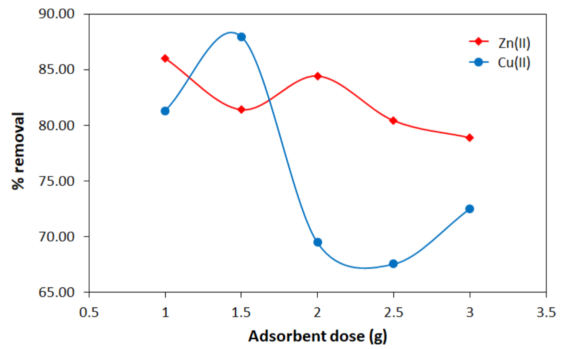

Figure 4. Effect of magnetic modified biosorbent doses on the removal percentages of Cu(II) and Zn(II) with modification ratio of 1:2 (Zn) and 2:1 (Cu) at 30°C and initial concentration of 100 ppm.

Isothermal Adsorption Models of The Biosorbents

Isothermal adsorption models were used to determine the interaction between Cu(II) and Zn(II) and the biosorbent surface. The isothermal adsorption models used in this study were Langmuir, Freundlich, Temkin and Dubinin Radushkevich. By using batch adsorption tests data the isotherm adsorption models were plotted for each of adsorbents (native and magnetically modified corn cob biosorbent) and metals (i.e. Cu(II) and Zn(II)). Figures 5 and 6 show the plots of several isotherm adsorption models for Cu(II) and Zn(II) on magnetically modified corn cob biosorbent, respectively. Whereas, Figures 7 and 8 show the plots of several isotherm adsorption models for Cu(II) and Zn(II) on native corn cob biosorbent, respectively.

From the plots in Figures 5 - 8, the parameters for each isothermal adsorption model have been determined and are presented in Table 1. Additionally, as shown in above figures, the isotherm adsorption model which was most fitted with the experimental data was Freundlich model. Therefore, the Cu(II) and Zn (II) adsorption process using native corncobs and magnetically modified corncobs, all of them correspond to the Freundlich

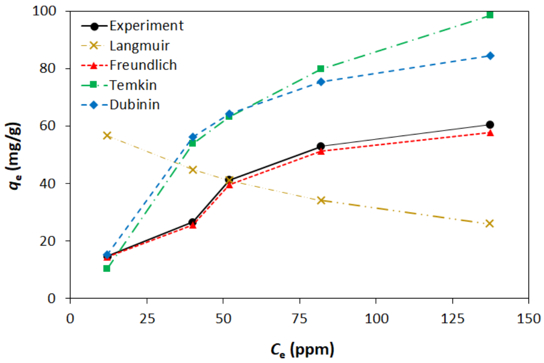

Figure 5. Isotherm adsorption models of Cu(II) on magnetically modified corn cob adsorbent in various models.

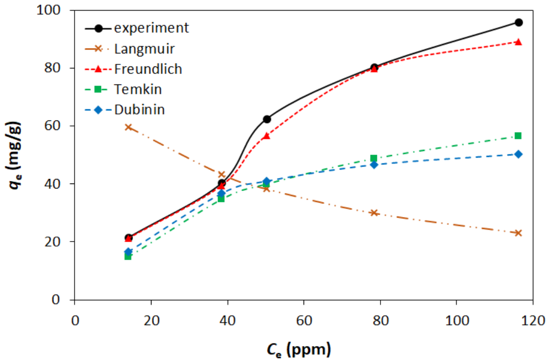

Figure 6. Isotherm adsorption models of Zn(II) on magnetically modified corn cob adsorbent in various models.

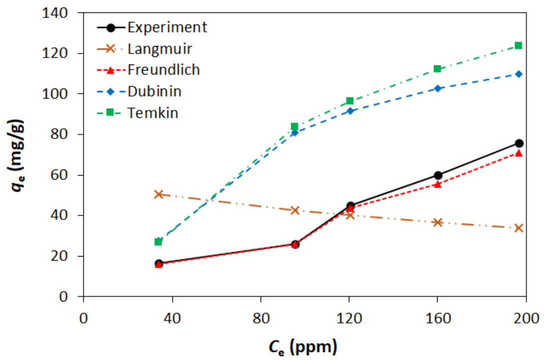

Figure 7. Isotherm adsorption models of Cu(II) on native corn cob adsorbent in various models.

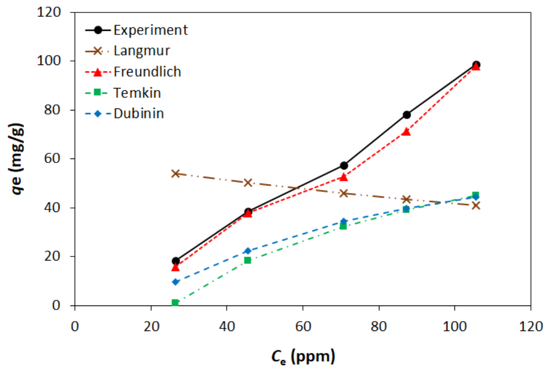

Figure 8. Isotherm adsorption models of Zn(II) on native corn cob adsorbent in various models.

Table 2. Parameters of isotherm adsorption models of Cu(II) and Zn(II) on native corn cobs and magnetically modified corncobs biosorbent.

	Magnetic corn cob		Native corn cob	
	Zn	Cu	Zn	Cu
		Langmuir		
Q_m (mg/g)	63.93	75.76	56.08	60.48
K_L (L/mg)	0.011	0.020	0.003	0.005
		Freundlich		
n	1.36	1.62	0.84	1.16
K_f(mg/g)	3.09	3.17	0.39	0.70
		Temkin		
A (L/g)	0.11	0.15	0.05	0.04
B (J/mol)	36.13	19.76	55.13	31.73
		Dubinin Radushkevich		
q_s (mg/g)	100.31	59.01	147.16	74.79
K_{ad} (mol²/kJ²)	0.01	0.01	0.02	0.02

Table 3. Comparison of adsorption capacity (q_e, mg/g) of the native and magnetically modified corncobs (in this study) with biosorbent from other literatures.

Biomass	q_m (mg/g)		Reference
	Cu	Zn	
Magnetic corn cob	75.76	63.93	This study
Peanut hull	21.25		(Zhu et al., 2009)
Orange peel	63.00		(Guiza, 2017)
Sawdust	42.40		(Ofomaja et al., 2010)
Banana peel char	75.99		[Ahmad et al, 2018]
Sugarcane waste		2.54	(Homagai et al., 2010)
Citric acid modified walnut		28.58	(Segovia-Sandoval et al., 2018)
Activated almond skin		5.54	Coruh, 2014

isothermal model. This isotherm model indicates that the adsorption process occurred multilayer with heterogeneous surfaces. This result was similar to the adsorption of heavy metal wastes by other biomass-based adsorbents (Saravanan et al., 2020). Furthermore, the adsorption capacity (q_e, mg/g) of the biosorbent studied in this research (i.e. native and magnetically modified corncobs) was compared with the biosorbent from other literatures.

Effect of temperatures on the adsorption efficiency

According to Mckay et al. (1989), the adsorption process of heavy metal such as Zn, Ni, Hg and Cu using biomass-based raw materials could be effective in a temperature range of 25°C to 60°C. Figure 9 shows the effect of temperatures (i.e. 30°C to 60°C) on the adsorption of Zn(II) and Cu(II) using magnetically modified corn cobs biosorbent. The removal percentage for both heavy metals (i.e. Cu(II) and Zn(II)) decreased at a temperature of 40°C. This was likely caused by the weakening of the binding energy between the adsorbent and the adsorbate (L., Zhao, et. Al., 2010) at 40°C and increasing again at 50°C and ends with saturation at 60°C. The optimum temperature in this adsorption process occurred at

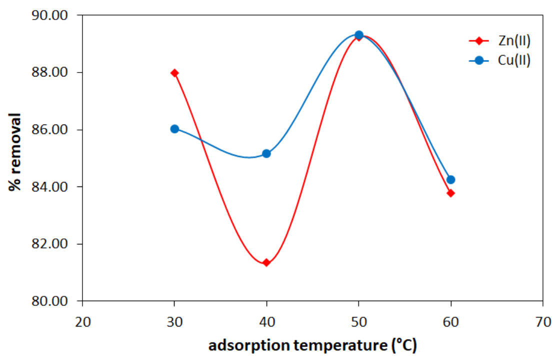

Figure 9. The effect of the adsorption temperature on the removal percentage of Cu(II) (with an adsorbent dose of 1.5 g and 2:1 modification ratio) and Zn(II) (with a 1 g adsorbent dose and 1:2 modification ratio) at the initial synthetic waste concentration of 100 ppm.

temperature of 50°C, because the binding energy between the adsorbent and adsorbate run very well at 50°C.

CONCLUSION

Magnetic modification of corn cobs based biosorbent using $Cl_3.7H_2O$ as magnetic modifier has increased the adsorption capability of Cu(II)) and Zn(II) from the synthetic wastewater. The optimum modification ratios were 1:2 and 2:1 Zn(II) and Cu(II), respectively. Additionally, the adsorption process of both heavy metals took place optimally at a temperature of 50°C with the adsorbent dose being fed were 1 gram and 1.5 grams for Cu and Zn. The highest adsorption percentages for Zn(II) and Cu(II) uptake process were 89.3% and 89.2%. The adsorption process of Zn(II) and Cu(II) by modified corn cobs biosorbent was in accordance with the Freundlich isothermal adsorption model.

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