



THE ADSORPTION KINETICS OF Cu(II) AND Cr(III) BY H₃PO₄ ACTIVATED CARBON MADE FROM MARIGOLD STEMS

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ARTICLE INFO

Article History:

Received 18th October, 2017

Received in revised form 10th

November, 2017

Accepted 06th December, 2017

Published online 28th January, 2018

Key words:

Activated Carbon, Adsorption, Cr(III), Cu(II), kinetics, marigold stems

ABSTRACT

This paper discusses the adsorption of Cu(II) and Cr(III) by H₃PO₄ activated carbon made from marigold stems. The objective of this research was to determine the optimum condition of the adsorption by the activated carbon in terms of contact time, adsorption isotherm, and pH, as well as the kinetics of the adsorption of the two metals followed by determining the adsorption capacity at the optimum conditions obtained. All metals measurements were performed by the use of atomic absorption spectrophotometer (AAS). It was found that the optimum contact time for Cu(II) and Cr(III) adsorption occurred at adsorption time for 40 minutes. The adsorption isotherms of activated carbon to both metal ions follow the isotherm pattern of L-type (Langmuir isotherm). The adsorption kinetics patterns for Cu(II) and Cr(III) adsorptions follow the kinetics of second order with adsorption rate constant of 3.09×10^{-5} and $2.49 \times 10^{-5} \text{ min}^{-1} \text{ ppm}^{-1}$, respectively. The optimum adsorption of the metals occurred at pH 2. The adsorption capacity of the activated carbon to Cu(II) and Cr(III) at the optimum conditions were of 0.2015 mg/g and 0.2259 mg/g, respectively. Under the optimum conditions, the activated carbon could decrease the Cu(II) and Cr(III) contents by 23.10% and 27.77%, respectively.

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INTRODUCTION

The waste of marigold stems is a biomass that can be used as the basic ingredient of activated carbon through pyrolysis or carbonization followed by activation process. Various biomass contained materials such as coconut bark (Ramdja *et al.*, 2008), acacia skin (Fausiah, 2009), corn stalks (Suhendra and Gunawan, 2010), bananas stems (Widihati, 2012), grass (Kalyani, 2013), skin of coffee grains (Purnomo, 2010), bamboo (Suheryanto *et al.*, 2013), cassava skin (Soetomo, 2012), and many others have been reported to be used to make activated carbon (Dean, 1999). Marigold of the varieties of *Tagetes patula* grown in a regions with temperatures of 20° - 30°C contain various minerals such as N, P, K, Ca, Mg, S, Al, B, Cu Fe, Mn, Mo, Na, Zn and C. Among all, carbon (C) is the highest content which is of 42 - 44% (van Lersel, 2006), hence the presence of this high enough carbon allows marigold plant waste to be utilized as the basic ingredient of activated carbon which can then be applied in reducing the contents of various pollutants such as methylene blue and naphthol yellow (Purnomo, 2010), phenol (Pambayun *et al.*, 2013), and various heavy metals (Singanan and Peters, 2013). Activated carbon can be used to adsorb substances derived from both liquid and gas phases.

Activation of carbon can be done physically or chemically, such as by heating or with the addition of chemicals so that the pores are open. Activated carbon can absorb anything that is in contact with the carbon (Mars and Reinoso, 2006). This is because of that the structure of the activated carbon is an amorphous carbon composed largely of free carbon and has a large surface. The surface area of activated carbon ranges from 300-3500 m²/gram and this corresponds to the internal pore structure which causes the activated carbon to have properties as an adsorbent. Qin *et al.* (2014) has successfully demonstrated the use of phosphoric acid as the chemical activator which was added at the time of carbonization of the marigold stems.

In the previous study, carbonization of marigold stems at a temperature of 300°C for 90 minutes (Siaka *et al.*, 2016) and activation with as much as 25 mL of 15% H₃PO₄ to each gram of the carbon, added after the carbon formed, (Sahara *et al.*, 2017) has proven to produce activated carbon with characteristics that meet the quality of Indonesian National Standard (SNI 06-3730 – 1995) concerning to the technical activated carbon. The characteristics examined included the contents of water, volatile compounds, ash and carbon, as well as the adsorption capacities to iodine and methylene blue.

From the discussion above, in this study the application of H₃PO₄ activated carbon for reducing the content of Cu(II) and Cr(III) was carried out. Prior to the analysis, the optimum

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adsorption conditions such as the contact time, adsorption isotherm, and pH, as well as the kinetics of the absorption of the two metals were investigated.

Experimental

Materials and Equipment

The object of the research was the H₃PO₄ activated carbon made from marigold stems (*Tagetes erecta*) which was collected from "Bali Gemitir Plantation" in the Region of Baturiti, Tabanan, Bali-Indonesia. The activated carbon was prepared by carbonizing the marigold stems at 300°C for 90 minutes, followed by grinding and sieving it into fine powdered of 250 – 150 μm (Siaka *et al.*, 2016). After that, each gram of the carbon formed was activated by adding 25 mL of 15% H₃PO₄ to 1 g of carbon and letting it to stay for 24 hours (Sahara *et al.*, 2017).

The chemicals used were of analytical reagent grade: H₃PO₄, CuSO₄.5H₂O, CrCl₃.6H₂O, HNO₃. The filtrations were carried out with the use of Whatman paper no. 12

The equipment used were analytical balance, glass tools, magnetic stirrer, and the Atomic Absorption Spectrophotometer Shimadzu A-7000

METHODS

Optimization of Cu(II) and Cr(III) Absorption Conditions with the Activated Carbon

Contact time determination

A half gram of activated carbon was put into a 100 mL Erlenmeyer flasks and then 25 mL of the mixture of Cu(II) and Cr(III) of 25 mg/L was added and stirred with magnetic stirrer for 10 minutes. The mixture was then filtered, the absorbances of both metal ions were measured with AAS. The procedure was also repeated for 20, 30, 40, 60, 90, 120 minutes of contact times.

Isotherm adsorption determination

Into 5 Erlenmeyer flasks it was filled each with 0.5 g of activated carbon then added with 25 mL of mixed Cu(II) and Cr(III) solution with various concentrations of 1, 2, 5, 10, and 20 mg/L. The mixtures were then stirred with a magnetic stirrer for the optimum contact time. The mixture was then filtered, the absorbances of both metal ions were then measured with AAS.

Determination of the adsorption kinetics

Each of 9 Erlenmeyer flasks of 100 mL was filled with 0.5 g of activated carbon, then added with 25 ml of Cu(II) and Cr(III) mixture with a concentration of 10 mg/L (obtained from the determination of adsorption isotherm). The mixtures were then stirred with a magnetic stirrer for 0, 3, 5, 10, 15, 25, 35, 40 and 60 minutes. The solutions were filtered and then the absorbances of both metal ions were measured with AAS. The reaction kinetics could be determined by drawing a plot between CA with variations of time or plot between 1/CA and time.

Effect of pH

It was prepared 4 Erlenmeyer flasks, each was added with 0.5 g of activated carbon and added 10 mL of buffer solution pH 2, 4, 7 and 11 respectively. Every flask was added with 25 mL

of Cu(II) and Cr(III) of 10 mg/L. The mixtures were then stirred with magnetic stirrer for the optimum contact time. The solutions were filtered, then the absorbance of both metal ions was measured with AAS.

Determining the adsorption capacity (adsorption power) of activated carbon

One gram of activated carbon was put into a 100 mL Erlenmeyer flask and then 50 mL of 10 mg/L mixture of Cu(II) and Cr(III) in 0.01 M HNO₃ or pH 2 (obtained from pH optimization) was added. The mixture was stirred at the optimum contact time, then the solution was filtered and the absorbance of the two metal ions was measured with AAS.

Application of the active carbon for the absorption of Cu(II) and Cr(III) in the liquid waste of a garment waste All optimum conditions obtained were applied to the waste sample collected from a garment company in Gianyar - Bali - Indonesia.

RESULTS AND DISCUSSION

Optimization of Cu(II) and Cr(III) Absorption Conditions

Contact time determination

The purpose of the determination of adsorption contact time is to find out the minimum time required by the adsorbent to adsorb maximum adsorbate until the saturation state is reached. The saturation state is achieved when the adsorbent reacted with the metal ions passes the equilibrium time so that the adsorbent is no longer able to adsorb (Castelan, 1982). Figure 1 shows the relationship between the amount of Cu(II) and Cr(III) adsorbed by the activated carbon against the contact time.

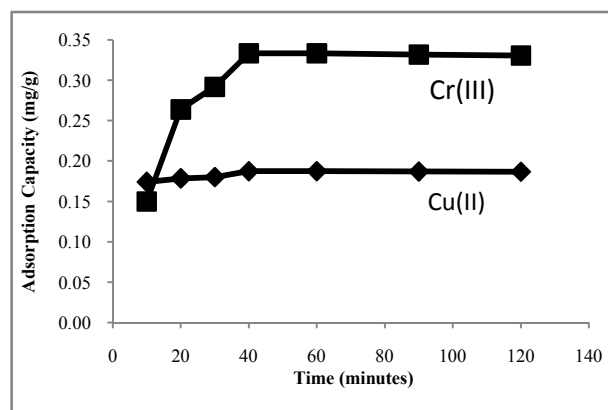


Figure 1 Correlation between contact time and adsorption capacity

It can be seen that the adsorption capacity of activated carbon from marigold stems to Cu(II) and Cr(III) generally increased as the interaction time increased. This increase lasted from 10 to 40 minutes of adsorption, and then after 40 minutes the adsorption took place almost constant. This may be due to that after 40-minutes equilibrium state, the interaction of the two metal ions with the activated carbon is getting weaker (physical adsorption) so that the two metal ions tend to remain in the solution. Therefore, the absorption time of 40-minutes was chosen as the optimal contact time and applied to the next parameters optimization. The absorption capacity of the activated carbon for Cu(II) and Cr(III) on adsorption for 40 minutes was 0.19 mg/g and 0.33 mg/g, respectively.

Isotherm adsorption determination

By determining the adsorption isotherm, it can be seen the relationship between the amount of metal ions adsorbed at various concentrations at room temperature and the adsorption capacity so that the isotherm absorption pattern can be established. Figure 2 shows the absorption capacity of activated carbon to various concentrations of Cu(II) and Cr(III) with the adsorption at equilibrium time of 40 minutes. From the figure it can be seen that the adsorption isotherm of the adsorbent on Cu(II) and Cr(III) followed the L-type adsorption isotherm pattern (Langmuir isotherm) (Atkins, 2006) which shows a relatively high affinity between the adsorbents with both metal ions at the beginning and then decreases slowly at higher metals concentrations.

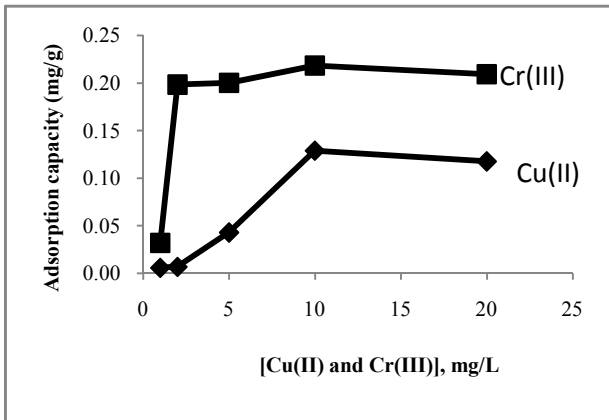


Figure 2 Correlation between adsorption capacity and metals concentration

The Langmuir isotherm is the simplest physically plausible isotherm which is based on three assumptions, namely that the adsorption cannot proceed beyond monolayer coverage, all sites are equivalent and the surface is uniform as well as the ability of a molecule to adsorb at a given site is independent of the occupation of neighbouring sites. It was observed that with increasing the concentrations of the adsorbates interacted, the amount of Cu(II) and Cr(III) adsorbed by each gram of activated carbon increased to the optimum level which was of 10 mg/L. Above this concentration the adsorption began to decline.

Determination of absorption kinetics

Kinetics adsorption is one of the important factors in the adsorption process as it shows the rate of adsorption by the adsorbent to the adsorbate. Figure 3 shows the first-order

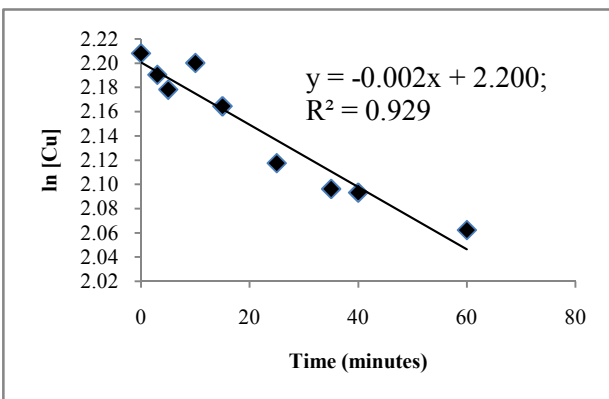


Figure 3 First order kinetics of Cu(II) adsorption by activated carbon

kinetics for the adsorption of Cu(II) by the activated carbon where $y = -0.002x + 2.200$ with $R^2 = 0.929$, while Figure 4 shows the second-order kinetics to Cu(II) where $y = 3.09 \times 10^{-5}x + 0.110$ with $R^2 = 0.965$.

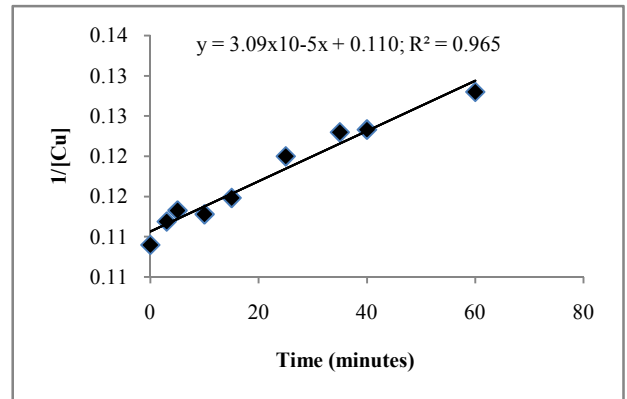


Figure 4 Second order kinetics of Cu(II) adsorption by activated carbon

Figure 5 shows the first-order kinetics for the adsorption of Cr(III) where $y = -0.002x + 2.261$ with $R^2 = 0.950$, while Figure 6 shows the second-order kinetics of adsorption by the activated carbon to Cr(III) where $y = 2.49 \times 10^{-5}x + 0.104$ with $R^2 = 0.972$. According to Figures 3-6, it can be concluded that the adsorption kinetics of Cu(II) and Cr(III) by activated carbon from marigold stems followed the second order kinetics. This can be seen from the linearity of the curve (R^2 value) in which the linear correlation coefficient of the 2nd order curve is greater than the first order curve. The values of the adsorption rate constant (slope (k)) based on the equations of the second order above for Cu(II) and Cr(III) are 3.09×10^{-5} and $2.49 \times 10^{-5} \text{ min}^{-1} \text{ ppm}^{-1}$.

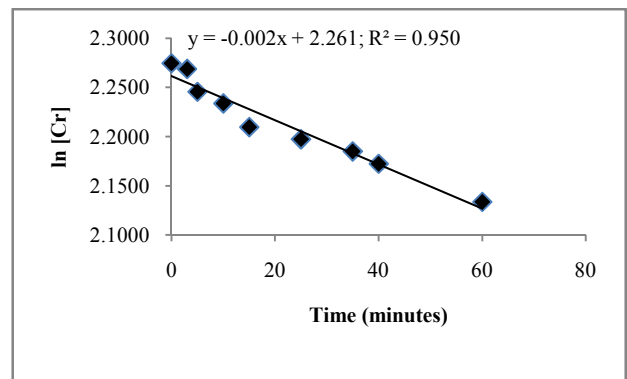


Figure 5 First order kinetics of Cr(III) adsorption by activated carbon

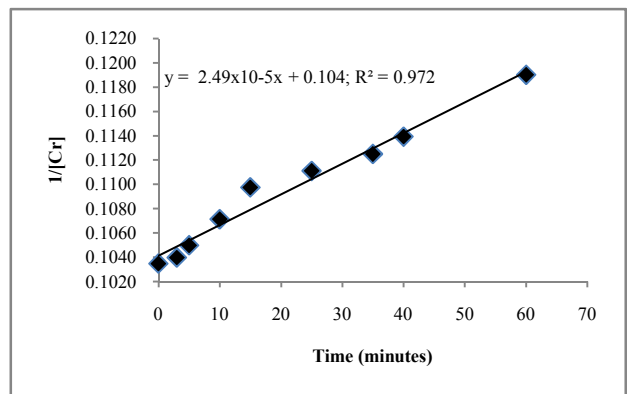


Figure 6 Second order kinetics of Cr(III) adsorption by activated carbon

Determining the effect of pH on Adsorption of Cu(II) and Cr(III)

Figure 7 shows the effect of pH on Cu(II) and Cr(III) adsorption by the activated carbon. From the figure it can be seen that the highest adsorption of Cu(II) and Cr(III) occurred at pH 2 which was of 0.20 mg/g and 0.22 mg/g, respectively. The higher the pH value, the metal adsorption ability decreases. At high pH there is precipitation of metal ions into hydroxide which reduces the solubility of the metal ions in the solution resulting in the decrease in the number of metal ions that can be adsorbed by the adsorbent surface. In addition, at high pH the concentration of OH-solution is also high because metal ions are more readily binding to OH-than to bind to the adsorbent. The high adsorption capacity at pH 11 can be caused by the high existence of precipitated metals as their hydroxides and as a consequence, there was small amount of metals in the filtrate measured.

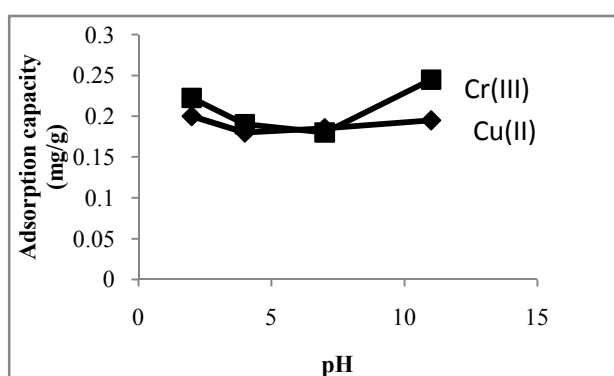


Figure 7 Correlation between pH and adsorption capacity of activated carbon to Cu(II) dan Cr(III)

Adsorption capacity determination

By applying the established conditions for the adsorption of Cu(II) and Cr(III), namely contact time of 40 minutes, both metals concentration of 10 mg/L and pH 2, the adsorption capacity of the activated carbon to Cu(II) and Cr(II) were found to be $0.2015 \pm 0.89 \times 10^{-3}$ mg/g and 0.2259 ± 0.02 mg/g, respectively.

Application of the active carbon for the absorption of Cu(II) and Cr(III) in the liquid waste of a garment waste

The activated carbon made from marigold stems obtained in this study has been applied to adsorb Cu(II) and Cr(III) in waste water collected from a garment company in the Gianyar region-Bali-Indonesia. The results obtained are presented in Table1.

Table 1 Application of the Activated Carbon to Liquid Waste of Garment Company

Repeation	[Cu(II)], mg/L		[Cr(III)], mg/L	
	Initial Concentration	With Activated Carbon	Initial Concentration	With Activated Carbon
1	5.7572	4.4906	0.4650	0.3550
2	6.0244	4.6000	0.4670	0.3755
3	6.2560	4.7797	0.4595	0.3346
Average	6.0125 ± 0.17	4.6234 ± 0.10	$0.4638 \pm 0.29 \times 10^{-2}$	0.3550 ± 0.01

From the table it can be seen that the use of the activated carbon as an adsorbent could decrease Cu(II) and Cr(III) contents by 23.10% and 27.77% respectively.

CONCLUSIONS AND SUGGESTION

From the study above, it can be concluded that the optimum adsorption conditions for Cu(II) and Cr(III) adsorptions by activated carbon made from marigold stems are as follows: the contact time was 40 minutes, adsorption isotherms for Cu(II) and Cr(III) followed the L-type adsorption isotherms (Langmuir isotherms) and the optimum adsorptions occurred at pH 2. The adsorption kinetics pattern for Cu(II) and Cr(III) adsorption were of second order kinetics with a rate constant of 3.09×10^{-5} and 2.49×10^{-5} minutes⁻¹ppm⁻¹, respectively. Under the optimum conditions, the adsorption capacities of the activated carbon to Cu(II) and Cr(III) were 0.2015 mg/g and 0.2259 mg/g, respectively, while the application of the activated carbon could reduce the content of Cu(II) and Cr(III) by 23% and 27.77%, respectively.

Because of that the activated carbon was proven to decrease both metals contents in waste water, the carbon may be applied to the other waste water samples or to adsorb other pollutants such as Pb(II), Cd(II), etc.

Acknowledgements

The authors would like to thank The Board for Research and Community Services Udayana University for providing the research grant through the scheme of Hibah Unggulan Program Study, so that this research could be well completed.

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How to cite this article:

Siaka I M and Sahara E (2018) ' The adsorption kinetics of Cu(II) and Cr(III) by H₃PO₄ activated carbon made from marigold stems', *International Journal of Current Advanced Research*, 07(1), pp. 8989-8993.
DOI: <http://dx.doi.org/10.24327/ijcar.2018.8993.1470>
