

Adsorption of lead(II) and copper(II) ions on rice husk activated carbon under sonication¹

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ABSTRACT

The effect of sonication on the adsorption of Pb^{2+} and Cu^{2+} ions on rice husk activated carbon has been conducted. This study was aimed to removal of Pb^{2+} and Cu^{2+} ions from aqueous solution by activated carbon under the influence of sonication. Surface characteristics of activated carbon showed that rice husk based activated carbon prepared at 400 °C and treated with $ZnCl_2$ 10% has better properties compared to the others prepared with difference conditions. The value of Langmuir model constant, b , for Cu^{2+} ion adsorption is -0.0362 (absence of sonication) and 0.1105 (presence of sonication), and for Pb^{2+} ion adsorption is -5.1508 (absence of sonication) and 1.0745 (presence of sonication). Those values suggest that ultrasonic irradiation positively affects the affinity of Pb^{2+} and Cu^{2+} ions towards the adsorbent. Maximum adsorption capacities increase in the presence of sonication. This can be seen on the value of a_m , Langmuir constant which represents the maximum adsorption capacity of adsorbent. The values of a_m for Cu^{2+} and Pb^{2+} adsorption changed from 1.0464 mg/g (absence) to 6.2775 mg/g (presence) and from 9.7561 mg/g (absence) to 16.5017 mg/g (presence), respectively. Those values suggest an increase in the adsorption capacity of activated carbon under sonication.

Keywords:

Activated carbon, rice husk, adsorption affinity, maximum adsorption capacity, ultrasound

1. INTRODUCTION

Environmental pollution due to the disposal of heavy metals and organic pollutants has been causing serious concern for the last few years [1-2]. Heavy metals are non-degradable to harmless end products, unlike organic pollutants, the majority of which are probably biodegradable. Heavy metals are toxic to aquatic ecosystems even in relatively low concentrations. Heavy metals, which are toxic to human beings and ecological environments, include chromium (Cr), copper (Cu), lead (Pb), and mercury (Hg), etc. These metals might be assimilated, stored and concentrated by human body, causing erythrocyte destruction, nausea, salivation, diarrhea, muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity [3-7].

Lead, which has been used by man for years, can be regarded as an important environmental contaminant. All compounds containing lead are considered as cumulative poisons that affect the gastrointestinal track, nervous system and sometimes both. The sources of lead in water are the effluents of processing industries, storage batteries, insecticides, plastic water pipes, food, beverages, ointments and medicinal concoctions for flavoring and sweetening. Environmental pollution due to copper is originated from mining, printed circuits, metallurgical, fiber production, pipe corrosion and metal plating industries. The other sources of copper pollution are industries of paper and pulp, petroleum refining and wood preserving. Agricultural activities such as fertilizers, fungicidal sprays and animal wastes can cause also copper pollution in water resources [3-7].

Removal of toxic or heavy metals from aqueous solutions can be carried out through several methods, such as chemical precipitation, membrane filtration, ion exchange, biosorption and adsorption [4]. Among those removal techniques of toxic or heavy metals, adsorption is the preferred method and gives the best results as it can be used to remove various types of toxic materials [1-7]. Commercial Activated Carbon (CAC) is the most widely employed adsorbent for the removal of toxic metals due to its effectiveness and high adsorption capacity; however, its use is still limited because of high operating costs. The need for regeneration and difficulty of separation from the wastewater after use are also major concerns associated with CAC. Many researchers have focused on finding non-conventional alternative adsorbents to reduce the cost of pollution treatment. Low-cost adsorbents are generally referred to non-hazardous waste produced from industry, agriculture, and biosorbents. Several lists and reviews of these types of adsorbent for pollutant removal have been made [1-2, 4]. In addition,

¹ Presented in International Symposium on Chemical and Bioprocess Engineering, Yogyakarta, 25-28 June 2013

the use of agricultural waste as adsorbent has attracted some researchers because: (1) it is available abundantly; (2) most of the types of agriculture waste are readily to be utilized and do not need a complex pretreatment step or activation process before applications; (3) regeneration of these adsorbents may not be necessary (unlike CAC, where regeneration is essential); and (4) less maintenance and supervision are required for the operation of the adsorption process [8-15]. However, use of these cheap alternatives for pollutant treatment is still limited because both insufficient documentation in real wastewater systems and the necessity of post-usage disposal. The employment of rice husk waste for the treatment of wastewater is a win-win strategy because it does not only convert the waste into a helpful material but it also prevents on-site burning of the waste, saves on disposal costs, and reduce CO₂ emission [1-4, 8-9]. Disadvantage of biosorbents, that is often found, is the relatively low adsorbing capacity. However, in some cases, the adsorption capacity can be improved by activation, surface modification, and sonication. The use of activated carbons from plant materials is also often suffered from the low adsorption rate because of their microporous structures and long diffusion path through solid particles of adsorbents [16-18].

The effect of sonication has been studied to exhibit several effects in solid-liquid systems such as the increase of mass transfer rate, the enhancement of the surface area by many micro-cracks formation on the surface of solid and the clean-up of solid particle surfaces [19-28]. The effect of ultrasound on the adsorption/desorption processes has been previously studied and some controversial effects have been found [16, 20-23]. Nevertheless, there is less information in the literature about the removal of heavy metal ions from aqueous solution by adsorption under the influence of ultrasonic irradiation [20-23].

The objectives of the current study was aimed to removal of Cu(II) and Pb(II) ions from an aqueous solution by adsorption onto the activated carbon obtained from rice husk under the influence of sonication. The models of Cu(II) and Pb(II) adsorption will be evaluated to observe the effects of ultrasound on the adsorption of both metals onto the rice husk based activated carbon, and finally to choose optimal adsorption condition.

2. MATERIALS AND METHODS

Materials: Rice husk (*Oryza satyfum* L.) was supplied from the south part of South Sulawesi (Bontomaero, Kecamatan Bajeng, Kabupaten Gowa). Fresh rice husk were washed several times with distilled water for the removal of surface impurities, dried at 100°C overnight (6h), crushed by a hammer mill and simultaneously carbonized in a muffle furnace at 300 and 400 C for 2h. Carbonized rice husk was then immersed into ZnCl₂ (10% w/v) for 24h. Afterwards, the granular activated carbon was washed three times with distilled water, dried at 110 C for 24h and stored in desiccators. Copper(II) acetate and lead(II)acetate, analytical reagent grade, were purchased from Merck Co. Distilled water was used to prepare aqueous solutions of copper(II) acetate and lead(II)acetate.

Material characterization: Surface characteristics of adsorbents were determined by Scanning Electron Microscope (SEM) (JEOL, JSM6510). Crystallinity analysis was carried out through X-Ray Diffraction method (XRD) (Shimadzu, XRD6000). Specific surface area, total pores volume, and pores size distribution were determined by N₂ adsorption method in a Gas Sorption Analyzer (Quantachrome, Autosorb iQ-MP).

Experimental set-up of sonication: The set-up consisted of an ultrasonic cleaner (Elmasonic S40H; total nominal power: 250 W; and internal dimensions: 300 x 220 x 155 mm), operating at 40 kHz frequency. The cleaner was filled with distilled water up to 1/3 of its volume (about 3.5 l). The temperature was controlled and maintained by water circulating from a thermostated bath by means of a pump. An Erlenmeyer flask (250 ml) used as adsorption vessel was fixed on a swinger (90 oscillations per minute). The copper(II) acetate and lead(II)acetate solutions (100 ml) and the adsorbent (1.0 g) were put into the flask fixed on the swinger.

Adsorption experiments: In these experiments, the initial copper(II) acetate and lead(II)acetate concentrations were in the range between 2 and 50 mg/l. In a preliminary equilibrium test under silent conditions applying the smallest (2 mg/l) and the highest (50 mol/l) copper(II) acetate and lead(II) acetate concentrations, it was established that the equilibrium was reached after 2 h. For sure, all equilibrium experiments lasted 3 h. After establishing equilibrium, a sample was taken from the flask and was centrifuged (1500 rpm for 5 min) for the removal of adsorbent particles. The Cu(II) and Pb(II) concentrations in the supernatant were measured by Atomic Absorption Spectrophotometer (AAS) Bulk Scientific Model 205VGP. The amount of Cu(II) and Pb(II) ions adsorbed was calculated from the mass balance equation (Equation 1).

$$q = \frac{(C_0 - C)V}{m_a} \quad (1)$$

Where q is the amount of ions adsorbed at time t ; C_0 and C are the initial ions concentration and the ions concentration at time t , respectively; V is the volume of solution (=100 ml); and m_a is the amount of adsorbent (=1.0 g). For each sample, the ion concentrations were measured in triplicate and the mean value was used as the equilibrium one.

3. RESULTS AND DISCUSSION

Characterization of rice husk based activated carbon (RHAC): The activated carbon prepared from rice husk by carbonization at elevated temperature (300C and 400C) and salt impregnation ($ZnCl_2$; 10% w/v) for 24 h was characterized by standard methods (Table 1 and Figure 1). The highest specific surface area of RHAC was obtained at carbonization at 400C i.e. 284,963 m^2/g , and the total pore volume was 4,670E-01 cc/g. The active groups were formed due to the dissolution of many chemical bonds initially present in the rice husk through prolonged carbonization at elevated temperature. Immersion of RHAC into $ZnCl_2$ 10% solution for 24h has increased the specific surface area and total pore volume. Based on the SEM results, the surface structure of RHAC (carbonization at 400C and activation with $ZnCl_2$; 10% w/v) has a layered structure and pieces of pores compared to the other RHAC (Fig. 2). Activation can increase the number of pores as can be seen from Fig. 2(a) and 2(b), respectively. The number of pores is available more in Fig. 2(a) than 2(b). This explanation can also be connected to information from the specific surface area and total pore volume, where RHAC produced and activated at 400 C has the highest value of both parameters. Activation can also increase the values of specific surface area from 38,248 m^2/g to 115,282 m^2/g , and from 55,074 m^2/g to 284,963 m^2/g at 300 C and 400 C of activation, respectively.

Table 1 Specific surface area, pores radius and total pores volume of activated carbon. 300 A and 400 A were activated by $ZnCl_2$ (10% w/v) at 300C and 400C, respectively. 300 TA and 400 TA means without activation at the same temperature.

No	Sample name	Specific surface area (m^2/g)	Pore radius (Å)	Total pore volume (cc/g)
1	300 TA	38,248	1,735E+01	3,318E-02
2	300 A	115,282	1,821E+01	1,050E-01
3	400 TA	55,074	8,040E+01	2,214E-01
4	400 A	284,963	3,278E+01	4,670E-01

Table 2 Parameters of adsorption isotherms and linear correlation coefficient of both presence and absence of ultrasonic irradiation experiments.

Isotherm	Parameter	Absence (Cu^{2+})	Presence (Cu^{2+})	Absence (Pb^{2+})	Presence (Pb^{2+})
Langmuir	a_m (q_{max})	1,0464	6,2775	9,7561	16,5017
	b (adsorption affinity)	-0,0362	0,1105	-5,1508	1,0745
	R	0,7612	0,9906	0,9988	0,9927
Freundlich	k_F (adsorption capacity)	10,4372	2,0086	7,1717	9,4595
	n (adsorption intensity)	-2,6385	4,3497	13,1926	8,4459
	R	0,5614	0,9054	0,7864	0,7972

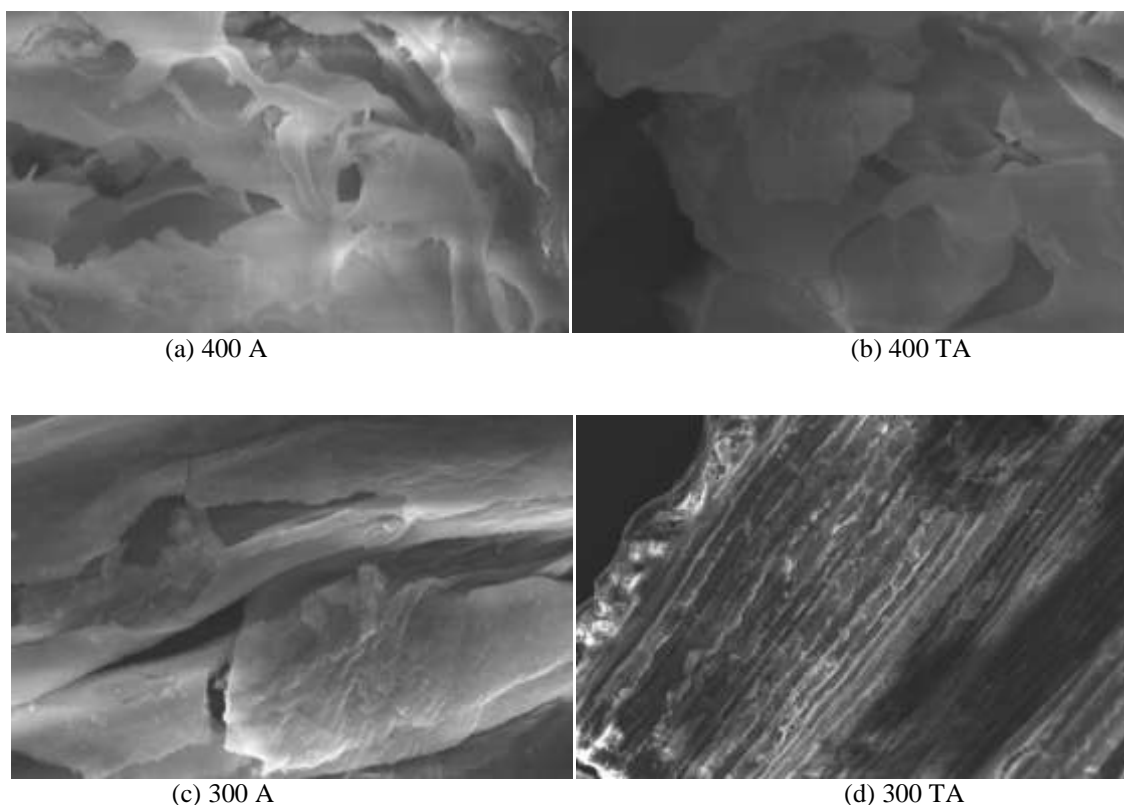


Figure 1. Surface characteristics of adsorbent determined by Scanning Electron Microscope (SEM). 300 A and 400 A were activated by $ZnCl_2$ (10% w/v) at 300C and 400C, respectively. 300 TA and 400 TA means without activation at the same temperatue.

In addition, as seen from Fig. 2, both adsorption isotherms for both metals are non-linear and seem to approach to the maximum values, except Pb(II) adsorption under sonication. Indication from the shape of the curves can be understood that several well-known models reported in the literature could be employed to explain the adsorption isotherms. Both Langmuir and Freundlich models are the most frequently used isotherms for adsorption studies [3-7, 10-16]. The Langmuir model can be applied to homogeneous sorption, where the sorption of each molecule is carried out onto monolayer surface and has equal sorption activation energy. The Freundlich model is an empiric isotherm model in nature. In this study, both adsorption isotherms were used to model the relationships between the amount of Cu(II) and Pb(II) ions adsorbed onto RHAC and its equilibrium concentration in solution in the absence and the presence of ultrasonic irradiation. Table 2 shows parameters of both adsorption isotherm models that were obtained in the presence and absence of ultrasonic irradiation. Nevertheless, when the Langmuir isotherm model was utilized in our experimental data, this model better fits both in the presence of ultrasound and its absence than with the Freundlich isotherm model. This can be seen in Table 2 when the corresponding linear correlation coefficients (R) are compared. The higher R-value for the Langmuir isotherm model than for the Freundlich isotherm model might be caused by homogeneous distribution of active sites of RHAC surface as it was explained in the case of Cu(II) ions removal by activated carbon from hazelnut shells under sonication [16].

The Langmuir constants a_m and b as well as the Freundlich constants k_F and n are also shown in Table 2. The Langmuir adsorption constant b defines the ratio of adsorption and desorption rate constants and is related to the free energy of adsorption. Its value represents the affinity of Cu(II) and Pb(II) ions to the adsorbent. When both values are compared, the values of b for the silent and the ultrasound-assisted adsorption, it can be concluded that ultrasound positively affected the affinity of Cu(II) and Pb(II) ions to the granular activated carbon as it was previously found for the adsorption of Cu(II) ions by activated carbon of hazelnut shell under sonication [16].

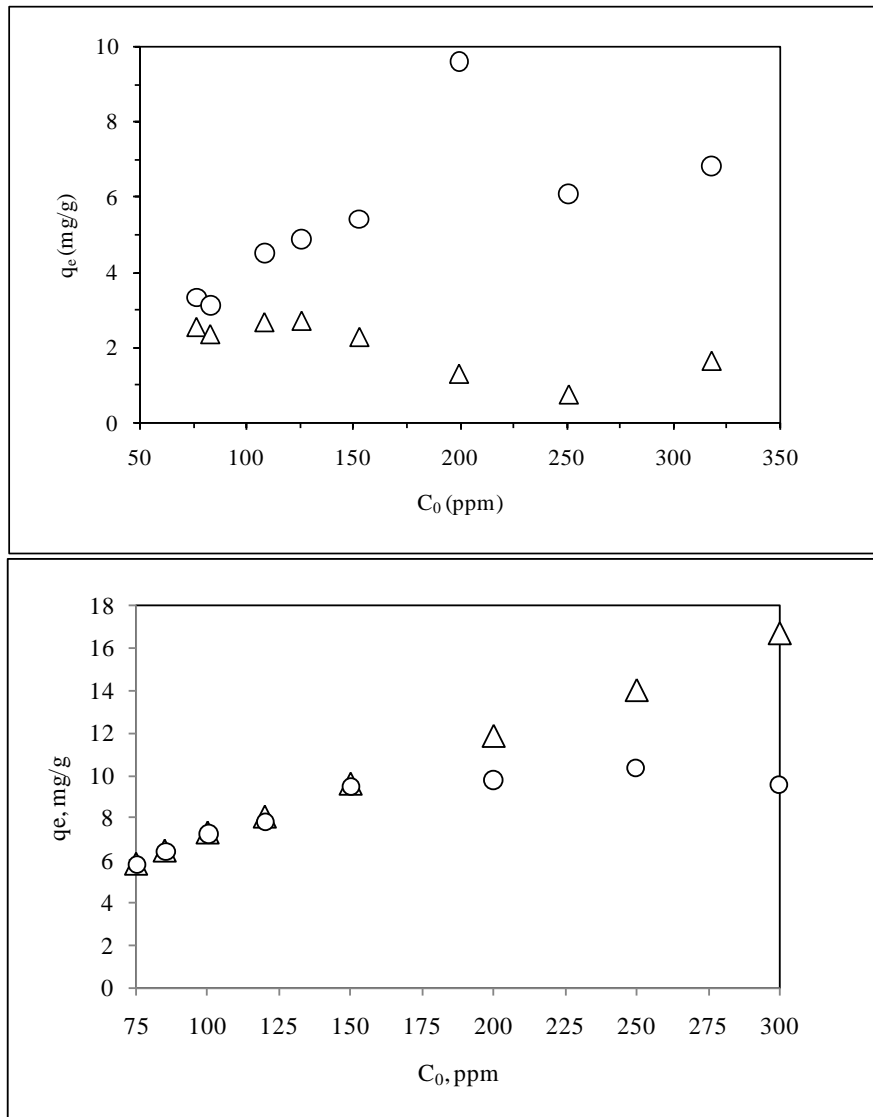


Figure 2. Adsorption isotherms of (upper) Cu^{2+} ions and (lower) Pb^{2+} ions on rice husk based activated carbon (O = presence of sonication, Δ = absence of sonication).

The difference conclusion was withdrawn from values of the Freundlich constant k_F , related to the adsorption capacity. The increase of k_F was only observed in adsorption of $Pb(II)$ ions under sonication, while in the case of $Cu(II)$ ions adsorption, sonication was decreasing the adsorption capacity of RHAC. The corresponding linear correlation coefficients (R) of $Cu(II)$ adsorption in the absence of sonication, however, is lower than the presence of sonication. The adsorption capacity of $Cu(II)$ ions by activated carbon of hazelnut shell was also greater in the presence of ultrasound than in the silent conditions [16]. This can be attributed to the cavitation effects which can increase the capability of the porous particle structure for $Cu(II)$ and $Pb(II)$ ions adsorption and/or the appearance of new sites of sorption by disruption of sorbent particles [16-28].

Maximum adsorption capacities for removal of $Cu(II)$ and $Pb(II)$ ions from aqueous solution by the granular activated carbon achieved in silent and ultrasound-assisted adsorption are 1.0464, 6.2775, 9.7561 and 16.5017 mg/g (calculated from the Langmuir isotherm model), respectively. Those values are much higher than that reported for the activated carbon obtained by steam activation of hazelnut shells under sonication [16]. This might be attributed to the specific surface area of the granular activated carbon of rice husk used in the present experiment.

5. CONCLUSION

Surface characteristics of RHAC prepared at 400C then impregnated with ZnCl₂ 10% are better than the other activated carbon prepared with the other conditions. When the values of *b* for the silent and the ultrasound-assisted adsorption are compared, it can be concluded that ultrasound positively affected the affinity of Cu(II) and Pb(II) ions to the surface of RHAC. The values for Cu²⁺ adsorption are 1.0464 mg/g and 6.2775 mg/g for the absence and presence of sonication, respectively, which suggests an increase (83%) in the adsorption capacity of activated carbon due to the ultrasonic irradiation. The values for Pb²⁺ adsorption are 9.7561 mg/g and 16.5017 mg/g for the absence and presence of sonication, respectively, which also suggests an increase (41%) in the adsorption capacity of activated carbon due to the ultrasonic irradiation. Langmuir adsorption isotherm model is better fits than the Freundlich model based on the values of corresponding linear correlation coefficients (R), both in the presence and absence of ultrasonic irradiation.

ACKNOWLEDGMENT

The author acknowledges for the financial support provided by Hasanuddin University (a Grant-in-Aid for Study Program Research DIPA Unhas No: 64/un4-lk.26/2012).

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