The Adsorption of Pb(II) Ions on Activated Carbon from Rice Husk, Irradiated by Ultrasonic Waves:Kinetic and Thermodynamics Studies

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Abstract
The research aim to determine the influence of variations of contact time, pH, and concentration on the adsorption of Pb(II); adsorption capacity; kinetic parameters (reaction order and the value of k) and thermodynamic parameters (Ea, ΔG, ΔH, ΔS) for the adsorption of Pb(II) using rice husk activated carbon were irradiated with and without ultrasonic waves. Method is making rice husk activated carbon, the effect of variation of time, pH, temperature and concentration. Analysis equation of pseudo first order reaction kinetics and pseudo second order, analysis equation of Langmuir and Freundlich, and thermodynamics. The method of analysis used in this research was the infra-red spectrophotometer (FT-IR), *the scanning electron microscopy* (SEM). The irradiated activated carbon adsorption capacity is 16.6667 mg/g and without irradiated is 9.8039 mg/g by Langmuir isotherm models. The optimum conditions for adsorption of Pb(II) at 50 minutes contact time, pH 5, temperature 40°C, whereas the concentration of Pb(II) 300 ppm adsorption is still experiencing. The result are suitable with the Langmuir isotherm models. Adsorption kinetics of Pb(II) were irradiated with ultrasonic waves followed the pseudo second order. Beside that thermodynamic parameters of ΔH, ΔS, ΔG and Ea are -11.1075 kJ $mole^{-1}$, -0.04192 kJ $mole^{-1}$ K, -4.55433 kJ $mole^{-1}$, 0.80213 kcal. $mole^{-1}$, respectively.
Keywords: adsorption, ultrasonic, metal Pb(II), activated carbon rice husk.

1. Introduction

Natural raw materials as agricultural waste are cheap and plentiful. They are known as biosorben being investigated widely to remove pollutants from the water. This study includes peat, pine bark, banana bark, rice bran, soybean, cotton seeds, peanut shells, walnut shells, rice husks, sawdust, wool fiber, orange peel, turmeric root and cocoa shells.

Adsorption process is expected to take heavy metal ions from water. Economically, this technique is more advantageous than others because of low cost and the absence of toxic side effects (Blais et al 2000). A drawback of biosorben is relatively low capacity. Adsorption capacity can be increased by activated carbon from agricultural waste. Carbon adsorption capacity is upgraded by using $ZnCl_2$ as activator. The research about activated carbon have done with other absorbat, some of them are phenol and 2-chlorophenol (Ansar 2012), methylene blue and eosin (Arnawaty 2012). Beside that methylene blue adsorption on various activated carbons including chaff rice has been investigated by (Kannan et al 2001), the use of activated carbon from sawdust and rice hulls for dye adsorption has also been studied (Malik 2002).

The use of activated carbon has a low adsorption due to the microstructure and diffusion path length through the solid particles. Increasing the adsorption capacity of the activated carbon can be done with irradiation by ultrasonic waves energy-producing chemical high. This occurs because a process of acoustic cavitation, namely the formation, growth and bubbles in a liquid solution. During the bubble solution, intense heating occurs at about 5000 °C, 500 atmosphere, and holding for a few microseconds (Suslick 1990). Ultrasonic waves cause mechanical effect on the reaction, for example, increasing the surface area through micro gap formation on solid surfaces, accelerating dissolution, or increasing the rate of mass transfer and cleaning the surface of solid particles (Suslick et al 1999).

Energy from the irradiation of ultrasonic waves will be used to increase the adsorption capacity of rice husk activated carbon to absorb heavy metals from the lead in solution. Studying will be conducted in the kinetics and thermodynamics of adsorption of lead metal by ultrasonic wave irradiation and the effect of variations in time, pH, temperature and concentration on the adsorption capacity of the activated carbon.

The purpose of this study were to determine the effect of variation of contact time, pH, and concentration on the adsorption of Pb(II), the adsorption capacity, the kinetic parameters (reaction order and the value of k) and thermodynamic parameters (Ea, ΔG, ΔH, ΔS) for the adsorption of Pb(II) using rice husk activated carbon were irradiated with and without ultrasonic waves. The expected result of this research is absorption Pb(II) process optimally by irradiated activated carbon with and without ultrasonic wave in optimum condition of contact time, pH, temperature and concentration. Adsorption capacity of activated carbon derived from rice husks to lead metal irradiated with ultrasonic waves is greater than the adsorption without ultrasonic waves. Addition, the study is expected to provide information about the kinetics of the adsorption process based on the adsorption rate and in order to achieve higher efficiency of the reaction, while in thermodynamics adsorption in terms of the energy involved in the adsorption process, whether or not the reactions spontaneous, endothermic or exothermic reaction.

2. Materials and methods

The materials were used in this research ie: the rice (*Oryza sativa* L) husk, $ZnCl_2$, $Pb(CH_3COO)_2$, $Na_2HPO_4.2H_2O$, citric acid ($C_6H_8O_7.H_2O$), H_3BO_3, KCl, NaOH, HNO_3, aquabidest, distilled water, Wathmann filter paper No.42.

2.1 Preparing Carbon From Rice Husk

Rice husk was washed and dried in oven at 110 °C, and than heated in a furnace at 400 °C for 2 hours.

2.2 Activation of Carbon by Using $Zncl_2$ Solution.

Carbon soaked in a solution of 10% ZnCl2 for 1 day. Carbon was washed with distilled water until neutral (approximately pH 7). Activated carbon is heated in a furnace at 400°C for 2 hours.

2.3 Effect Of Time, pH, Temperature and Concentration on Metal Adsorption Pb(II)

Time from 1 until 135 minute were done by activated carbon rice husk as much as 1 g was contacted with initial concentration solution of Pb(II) 50 mL, 250 ppm. This process was done by the aid of ultrasonic waves at 30°C and then filtered, the concentration of Pb(II) in the filtrate was analyzed by atomic absorption spectrophotometer (AAS). Adsorption with variation of pH (2-9), temperature (30-60°C) and concentration (75-300 ppm). Thermodynamic studies performed at 30 – 50 °C and concentration at 50-300 ppm.

Determining of Pb(II) adsorbed was calculated using the formula:

$$q_e = \frac{(C_0 - C) x V}{m} \quad (1)$$

q_e = amount of metal absorbed over a certain time (mg/g) C_0 = initial concentration of metal (mg/L)
C = concentration of metal after a certain time (mg/L)
V = Volume of solution of Pb(II) (L)
m = mass of activated carbon (g)

3. Results and discussion

3.1 Effect Of Time Variation In The Adsorption Of Pb(II)

The effect of time on the adsorbed amount of lead is presented in Figure 1. The amount of Pb(II) adsorbed by ultrasonic waves greater than without ultrasonic. Optimum contact time on the adsorption with ultrasonic waves is 50 minutes. A long time in the adsorption process of Pb(II) reached equilibrium showed physical interactions occurring. Adsorption of physics will continue to form multilayers at high pressure, but the low pressure and high temperature can be turned into desorption (Alberty & Silbey 1992).

3.2 Study Of Kinetics (Reaction Order And The Value Of k)

Adsorption process of Pb(II) with ultrasonic waves according to the pseudo-second-order kinetic model than the pseudo first-order kinetic model, indicating the rate of adsorption is influenced by the adsorbent and adsorbate. kinetics parameter reaction values can be seen in Table 1.

3.3 Effect Of Ph Variation On The Adsorption Of Pb(II)

Effect of pH on the adsorbed amount of lead is presented in Figure 2. Adsorbing Pb(II) by ultrasonic wave irradiation was greater than without irradiation and suitable with increasing pH. At pH 3-5, the adsorption of Pb(II) on irradiated activated carbon have increased. This happened because the amount of H^+ ions were reduced, so that the competition between metals Pb(II) with H^+ ions decreased and the surface of adsorbent was ionized by releasing H^+ ions and it became negative (Vasu 2008). The result was showed the electrostatic interactions between the surface of the adsorbent with Pb(II). The equilibrium was occurred at pH above five because Pb(II) started to sink at pH > 5, thereby reducing the amount of Pb(II) which could be adsorbed. The decrease was due to the rather high pH hydrolysis of lead had become $Pb(OH)^+$ (Ghazy et al. 2007). Because hydrolysis, lead positive charge wass reduced to +1 and make low interaction.

3.4 Effect Of Temperature Variation On The Adsorption Of Pb(II)

Effect of temperature on the adsorbed amount of lead is presented in Figure 3. At 30 – 40 °C an increase in the adsorption of Pb(II) on activated carbon were irradiated with ultrasonic waves, this can happen because at that temperature accelerate the adsorption process of Pb (II). The optimum temperature on adsorption of Pb(II) is 40 °C. At a temperature of 40 °C-50 °C Pb(II) adsorbed to experience equilibrium due to large energy generated from cavitation akuistik, whereas at 60 °C of Pb(II) adsorbed decreased due to adsorption at this temperature is exothermic so increase in temperature will reduce the ability of adsorption. In the adsorption process without ultrasonic at a temperature of 50 °C Pb(II) adsorbed to experience equilibrium.

3.5 Effect Of Varying The Concentration On The Adsorption Of Pb(II)

Effect of the concentration of the adsorbed amount of lead that is presented in figure 4. At various concentrations of Pb (II) adsorbed by ultrasonic wave irradiation was increasing. It indicates the magnitude of adsorption capacity of the activated carbon because the ultrasonic waves cause mechanical effect on the reaction.For example, increasing of the surface area through the establishment of a micro gap on solid surfaces, dissolution accelerating, or increasing of the rate of mass transfer and surface cleaning of solid particles (Suslick et al 1999). The equilibrium condition occur on adsorption without ultrasonic waves at 150 ppm.

3.6. Langmuir Adsorption Isotherm

Langmuir isotherm is based on the assumption that maximum adsorption corresponds to a single layer of adsorbate molecules on the surface, where the adsorption energy is constant and no molecules migration on the surface. Linear form of the Langmuir isotherm equation is shown from the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 . b} + \frac{C_e}{Q_0} \quad (2)$$

Where Ce is the equilibrium concentration (mg/L), qe is the amount of substance adsorbed per gram of adsorbent (mg/g), Qo and b are Langmuir constants declared in a row that the adsorption capacity and energy of adsorption (Periasamy et. al. 1995). Table 1 can be seen the adsorption process of Pb (II) with ultrasonic waves according to the Langmuir model of adsorption capacity at 16.6667 mg/g.

3.7. Study Of Thermodynamics (Ea, ΔG, ΔH, And ΔS)

Thermodynamic studies on the adsorption of metal Pb(II) with ultrasonic waves demonstrate the value of ΔH is negative. It means that the adsorption process is exothermic and can be predicted the amount of energy produced as heat. Negative value of ΔS is showed the system becomes more organized. The negative value of ΔG (less than 40 kJ/mol) is indicated that adsorption process can occur spontaneously and physical adsorption process. Physic adsorption involving are van der Waals forces and hydrogen bonding. In physical adsorption, the molecules are adsorbed on the surface with weak bonds. Adsorption is reversible so that the adsorbed molecules are easily removed again by lowering the gas pressure or solute concentration. Physical adsorption is affected by polarization, there is no sharing of electrons between the adsorbate to the surface, so there is no significant change in the electronic structure of the adsorbate. Adsorption energy generated in the physics of adsorption <40 kJ/mol. Enthalpy of the process is not enough for the termination of the bond so that the physically adsorbed species generally remained intact. Value of activation energy (Ea) indicates the size of the sensitivity of reaction rate to temperature changes.

3.8. infra-red spectrophotometer (FT-IR)

Results of analysis of activated carbon infrared spectra before and after interaction with Pb(II) with the irradiation of ultrasonic waves can be seen in Figure 5, and the difference is found in Table 2. After contact with Pb(II), the region at a wavelength of 3454.51 cm^{-1}, 1739.79 cm^{-1} and 1097.5 cm^{-1} absorption band is experiencing a shift that is not too big. A shift absorption bands amounted to less than 20, it indicates that the physical interaction caused by force van der waals.

3.9 Scanning Electron Microscopy (SEM)

Surface shape is one of the factors that play a role in the ability of an adsorbent to adsorb the adsorbate. To find the difference between the surface of the activated carbon used before and after adsorption of Pb (II) were irradiated with ultrasonic waves in this study it was characterized using Scanning Electron Microscopy (SEM). Characterization using SEM results showed that the surface structure of activated carbon before and after adsorption of Pb (II) obtained are different from each other.

Figure 6(a) shows the form of surface rice husk activated carbon, while Figure 6(b) show the surface of activated carbon after interaction with Pb (II) 250 ppm, for 50 minutes with ultrasonic waves. Activated carbon has a surface of shapes layered and holes that will improve the ability of activated carbon to adsorb Pb (II) because the hole is a gap that extends the surface of activated carbon to absorb the adsorbate.

4.Conclusion

Activated carbon rice husk can be used for metal adsorption of Pb(II). Activated carbon adsorption capacity is irradiated with ultrasonic waves are twice as much as than non irradiated ultrasonic waves at 50 minutes. The optimum conditions of metal adsorption Pb(II) at 50 minutes contact time, pH 5, 40°C, while the optimum concentration of metal Pb(II) is 300 ppm and follow The Langmuir isotherm models. Metal adsorption kinetics of Pb(II) were irradiated with ultrasonic waves followed the pseudo second order. Thermodynamic parameters were calculated ΔH, ΔS, ΔG, Ea are -11.1075 kJ $mole^{-1}$, -0.04192 kJ $mole^{-1}$ K, -4.55433 kJ $mole^{-1}$ and 0.80213 kcal. $mole^{-1}$.

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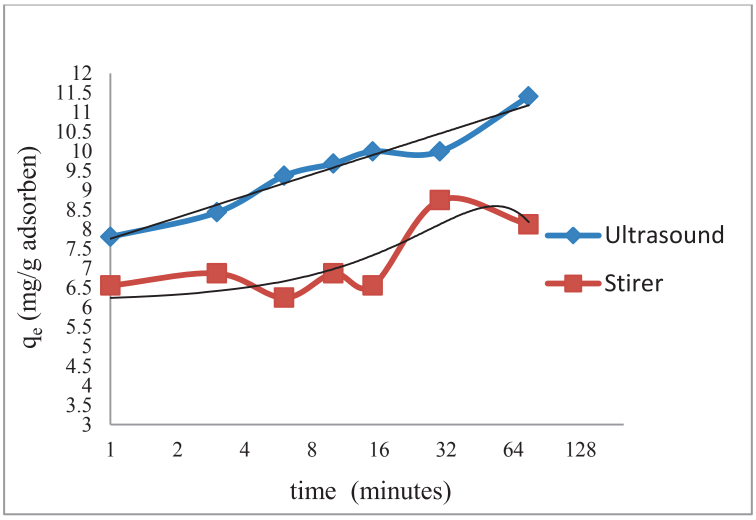


Figure 1. Graph the relationship between the variation of the contact time with the amount of metallic Pb (II) adsorbed by the activated carbon were irradiated with ultrasonic waves and without irradiation.

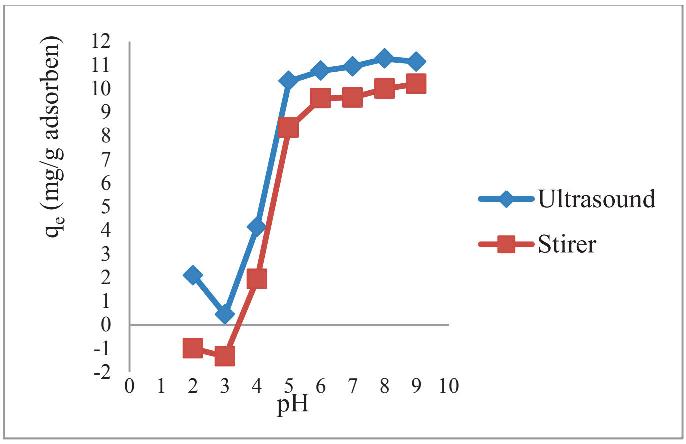


Figure 2. Graph the relationship between the variation of pH with the amount of metallic Pb (II) adsorbed by the activated carbon were irradiated by ultrasonic waves and without irradiation.

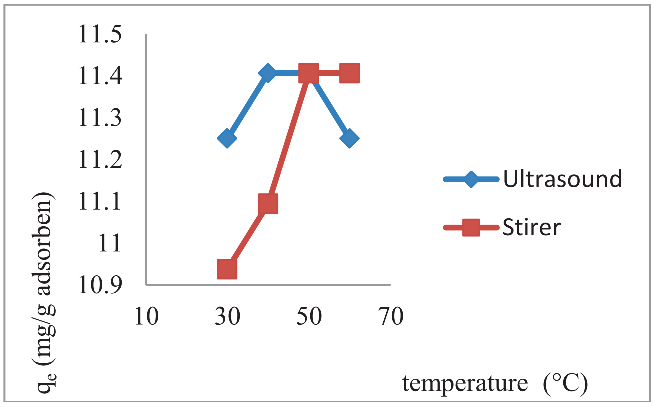


Figure 3. Graph the relationship between variation in temperature with the amount of metal Pb (II) adsorbed by the activated carbon were irradiated with ultrasonic waves and without irradiation.

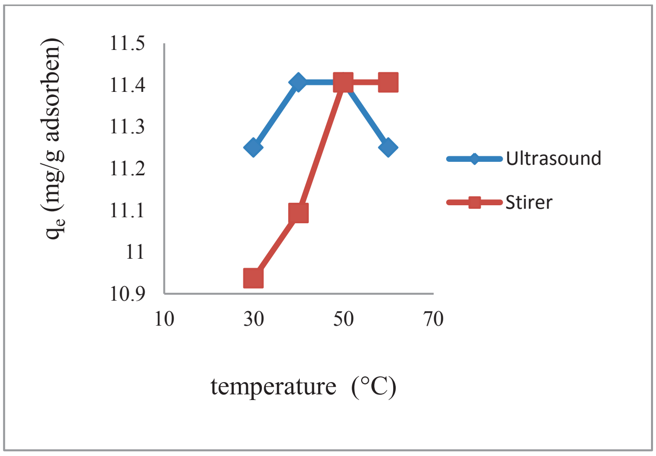


Figure 3. Graph the relationship between variation in temperature with the amount of metal Pb (II) adsorbed by the activated carbon were irradiated with ultrasonic waves and without irradiation.

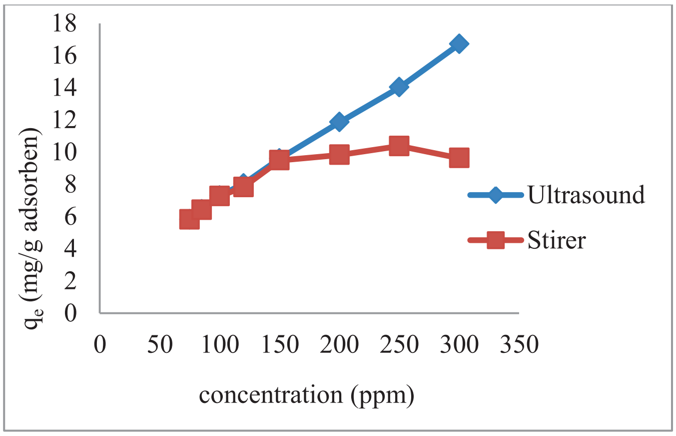


Figure 4. Graph the relationship between the variation of the concentration with the amount of metal Pb (II)

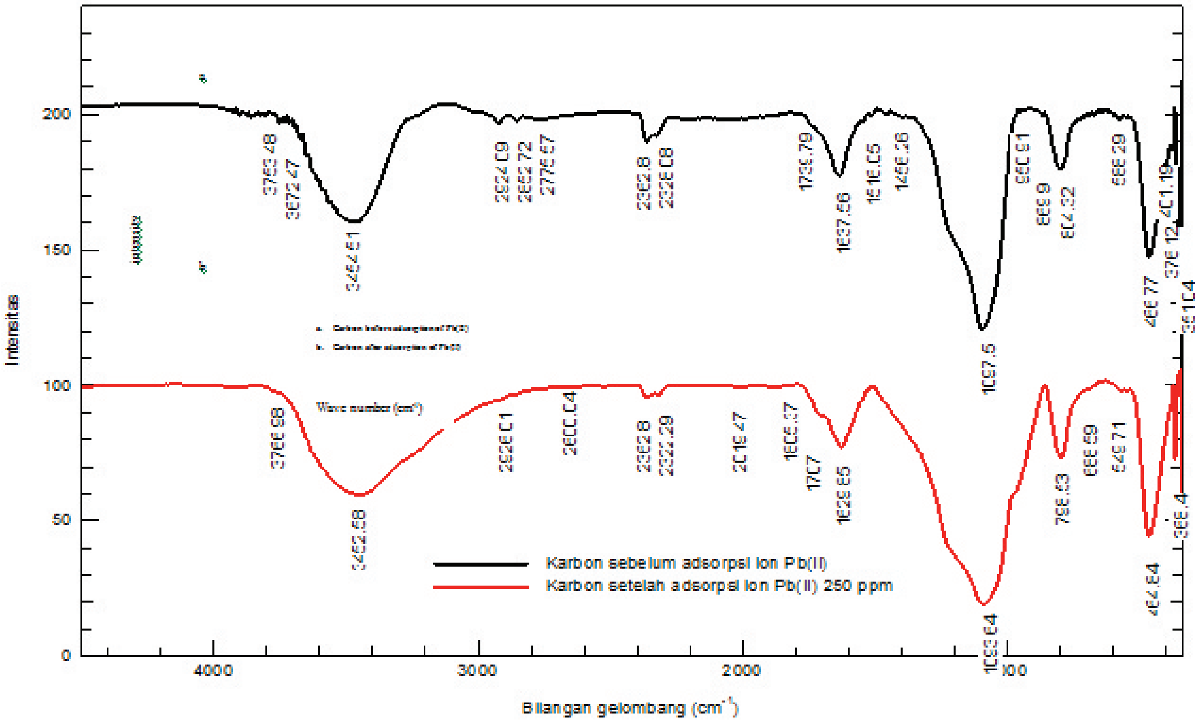
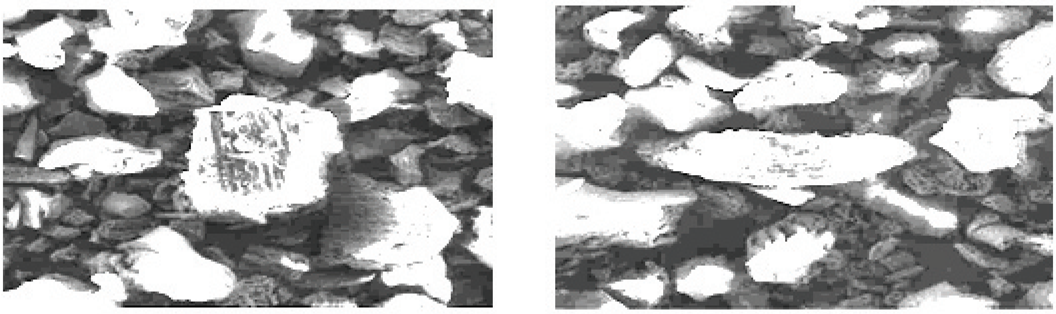


Figure 5. Infrared spectra before and after adsorption of Pb (II) with ultrasonic waves.



(a) (b)

Figure 6. SEM results (a) rice husk activated carbon (b) activated carbon – Pb

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Table 1. Langmuir models, Freundlich models, pseudo first-order kinetics, pseudo second-order and thermodynamic parameters for the adsorption of Pb (II).

Langmuir models parameters					
	Q_o (mg g^{-1})	b (l. mg^{-1})	R^2		
Pb (Ultrasonik)	16,66667	1,07	0.992		
Pb (tanpa Ultrasonik)	9,8039	-5,37	0,998		
Freundlich models parameters					
	n	K_F	R^2		
Pb (Ultrasonik)	8.4745	9.4406	0.797		
Pb (tanpa Ultrasonik)	13,3333	7,1614	0,78		
Pseudo first-order kinetics					
Pb	k_1 (min^{-1})	q_e (mg g^{-1})	R^2		
	-0.001	10.9375	0.023		
Pseudo second-order					
Pb	k_2 (g mg-1 min-1)	q_e (mg g^{-1})	R^2		
	0.04178	11.6279	0.999		
Thermodynamic parameters					
Pb	t (°C)	ΔH (kJ mole^{-1})	ΔS (kJ mole^{-1} K^{-1})	ΔG (kJ mole^{-1})	Ea (kcal. mole^{-1})
	30	-11,1075	-0.02163	-4.55433	0.80213
	35		-0.02444	-3.58082	
	40		-0.04192	2.013659	
	45		-0.01822	-5.31392	
	50		-0.02446	-3.20645	

Table 2. Comparison infrared spectra of rice husk activated carbon before adsorption and after adsorption of Pb(II) 250 ppm, for 50 minutes.

Wave number (cm^{-1})		functional groups
activated carbon	activated carbon - Pb	
3454,51	3452,58	-OH
2924,09	2926,01	-CH
1739,79	1707	-C=O
1637,56	1629,85	-N-H
1097,5	1093,64	-Si-O
804,32	798,5	Si-C