Study on the Removal of Pb(II) Ions from Aqueous Solution Using Chemically Modified Corn Cob

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ABSTRACT

Corn cob, a by-product of agricultural industry that is easily available in nature and low cost has been investigated as adsorbent in order to remove the Pb(II) ions from aqueous solution. Corn cob has been chemically modified with carbon disulfide, CS_2 *through xanthation process to enhance the adsorption capacity of Pb(II) ions. Batch experiments were carried out for further study on the effect of parameters such as pH, adsorbent dosage, initial metal ions concentration and contact time. The adsorption kinetic data was well described by pseudo-second order model and the adsorption isotherm indicate that Langmuir model fitted well the experiment data than Freundlich model. According to the Langmuir model, the calculated value of maximum adsorption capacities of Pb(II) ions* q_{max} *was 16.39 mg g-1. The characteristic of corn corb before and after being treated with xanthate, CCX (corn cob xhantate) was characterized by Fourier transform infrared (FTIR) spectroscopy. This study showed that CCX can be used as good adsorbent materials for Pb(II) removal from aqueous solution.*

Keywords: *corn cob, xanthation, adsorption kinetic, adsorption isotherm.*

Introduction

In the past few years, water pollution caused by heavy metal concentration into water bodies has appeared as a worldwide problem (Peng et al., 2009). The increase in industrial development and world population rates have led to high water pollution. The amounts of heavy metals in wastewaters have capability to endanger environmental and pose a serious impact on human health. Heavy metal such as lead is extremely hazardous to human health due to its carcinogenic activities. The Agency for Toxic Substances and Disease Registry (ATSDR) of the United States had listed lead metal as prioritized hazardous substances (Liu et al., 2012). In Malaysia, the Department of Environment (DOE) which was founded by the Ministry of Science, Technology and Environment (MOSTE) has enforced 0.01 mg/L as the national guideline for raw drinking water quality (DOE, 2012). This is because the existence of lead even in small amount in drinking water may result in many disorders like nephrite syndrome, anemia and hepatitis (Chakravarty et al., 2010). Exposure lead has been associated in very wide ranging health effects including weakness in fingers, ankles and at long term exposure causes impaired blood synthesis, hypertension, brain disorder and can cause miscarriage in pregnant women (Chakravarty et al., 2010). Therefore, it is crucial to control lead disposal into environment.

The hazardous heavy metals can be removed from the water body by applying conventional physical and chemical methods, such as coagulation, evaporation recovery, oxidation/reduction, filtration, precipitation, ion exchange, reverse osmosis and electrochemical treatment. Unfortunately, most of these conventional methods have contributed certain weaknesses such as high cost, complicated process and particularly viable at high concentration level of heavy metals (Ahmad et al., 2012).For these reasons, it is necessary to prepare low-cost and easily available adsorbent in removing toxic metal ions from wastewater. According to Surchi (2011), a low-cost adsorbent can be described as waste materials that available abundant in nature and requires only a few processing. One of the most abundant materials in nature is agricultural waste. In simple word, an agricultural waste is a residual material produced from poultry, livestock and also can be described as the residue of grains, fruits and vegetables. Increasing in agricultural sector consequently lead the amount of waste generated also increased.

The significance of this study is to find another alternative method in separating heavy metal ions from the aquatic ecosystem. Consequently, this study offers economical and inexpensive adsorbents because activated carbon, the most common used adsorbent in removing heavy metal is expensive. Besides that , corncob is also one of agricultural wastes from the sweet corn canning industry which is abundant and easily available. These corncob residues usually were burnt and disposed into environment without utilization. Therefore, it is hoped that this study would give a solution in overcoming the problem related to corncob waste disposal. The objectives of this study is to perform chemical treatment on corncob particularly xanthation process and evaluate its adsorption capacity for lead (II) ions and also to study kinetic and mechanism adsorption for removal of lead (II) ions by treated corncob.

Method

Chemicals and adsorbent treatment

Solution of lead (II) ions at different concentrations were prepared by doing appropriate dilution with deionized water from 1000mg/L $Pb(NO_3)_2$ stock solution purchased from Merck, Germany in order to obtain the desired concentrations used in the experiment. The treatment of corncob with xanthate was carried out according to Wing's procedure (Wing *et al.*, 1975). Corncob was washed several times with distilled water and dried in an oven at 80°C for 24 h. The products were cut into small pieces, crushed to powder form, and sieved to get several uniform particles sizes with the average of 75 – 355 μm. Corncob then was chemically modified as corncob xanthate. A 15 g of corncob powder were soaked into 200 mL (4.0 M) sodium hydroxide (NaOH) solution and stirred at room temperature for 2 h. Then 1 mL of carbon disulfide (CS2) solution was added to the mixture and the mixture was stirred for another 2 h. The products were allowed to settle for 30 min. The obtained product was washed with distilled water to remove excess alkali and dried in an oven overnight at 50°C for the further use. The dried adsorbent was kept in plastic containers and the xanthated corncob was designated as CCX.

Adsorbent characterization

The infrared spectrum of treated corncob was observed by using a Fourier transform infrared (FTIR) spectrophotometer. FTIR analysis was used in order to determine both the active groups present and compared the changes between the untreated and treated corncob in frequencies of the functional groups. The sample spectra were scanned within the wave number ranges of 400 – 4000 cm-1 at a resolution of 4 cm-1.

Batch experiments

Batch sorption experiment were conducted by mixing 0.1 g of adsorbents powder with 40 mL of Pb(II) solution in a 250mL Erlenmeyer flask on a thermal shaker at 250C and 120 rpm for 2 hours until equilibrium was reached. This process then was followed by centrifugation at 5000 rpm for 5 min to separate the adsorbent from the aqueous solution. After the agitation, the suspension were filtered using filter paper and the concentration of Pb(II) remaining in supernatant were analyzed by using atomic absorption spectroscopy (AAS).

Results and discussion

Adsorbent characterization

Variety of functional groups are expected to be presented in the adsorbent and change in the functional group after pretreatment is also expected. Thus, Fourier transform infrared spectrometer (FTIR) was used to observe the differences of adsorbent FTIR spectra for both before and after treatment. After undergo xanthation process, the FTIR spectra of CCX displayed several new adsorption peaks and some of disappearance peaks as given in Table 1.

Table 4.1 Comparison of FTIR spectra before and after treatment.

	Wavenumber cm^{-1}	
Functional group	**Before treatment (UCC)**	**After treatment (CCX)**
Overlapping of O-H and N-H stretching	3290	3316
Stretching of C-H	2919	2895
carboxyl groups	1727	
asymmetric of C=O	1626	1628
Stretching of C=S		1421
Stretching of C-S		1315
C-O stretching next to carbonyl group	1156	1156
Stretching of C-O-C	1034	1021
Stretching of C-S		894

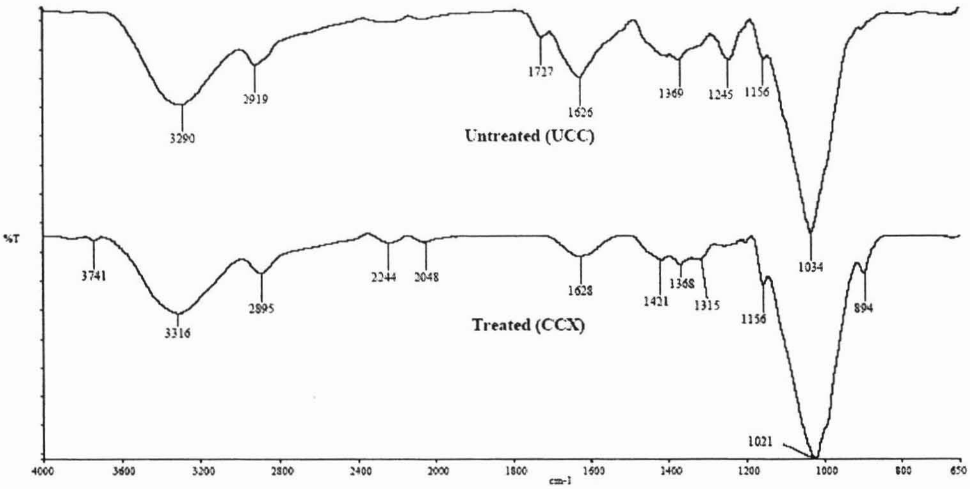

Figure4.1 FTIR spectra of untreated corncob (UCC) and treated corncob (CCX).

Figure 4.1 shows the FTIR spectra of untreated corncob UCC and the treated corncob,CCX. The broad and strong adsorption peaks ranging from 3200 cm-1 to 3600 cm-1 represented of O-H and N-H stretching vibration existence. There were two peaks in the region 2919 cm-1 and 2895 cm-1 which indicate methyl group asymmetric C-H stretching. Disappearance peak at 1727 cm-1 of untreated corncob may due to modification treatment which could suggest the carboxylic acid and ester groups were converted into carboxylate.

The existence peak at 1628 cm-1 could be represent C=O stretching in carbonylgroup. The new appearance adsorption peak at 1421 cm-1 confirms the existence of –C=S group. However, the unchanged peak at 1156 cm-1 indicates the C-O stretching next to carbonyl group. The shifted of strong peak at 1034 cm-1 to 1021 cm-1 propose the formation of C-O-C bond. The peak appeared at 894 cm-1 corresponding to C-S bond. Based on FTIR spectra analysis, it can be summarized that there were several appearance of new peaks and also disappearance of peaks after modification process. Therefore, the significant functional groups that participate in adsorption process were hydroxyl, amino, ether, and carboxylate groups.

Effect of pH

The pH value of the solution is considered as an important factor which greatly affects the uptakes metal studies. It significantly affects surface charge of sorbents and the ionic state of metals through the protonation and deprotonation process. Figure 4.2 clearly shows the effect of pH on adsorption capacity of lead (II) ions in solution. The curve indicates the adsorption of lead (II) ions increased from 10.57% to 99.06% with an increase in pH range from 2 to 5 but at pH 5 until 6 the uptake of ions becomes diminished. At pH 2, adsorption of lead ions was low because the concentration of H+ ions is high as the solution in an acidic condition. An excess of hydrogen ions in solution can cause a competition against lead ions for the binding sites on the surface of the adsorbent. However, at pH 1 which is in highly acidic condition, the adsorption of lead (II) ionsvery low due to protonation. The adsorbent become positively charge and lead (II) ions exist as cation thus resulting repulsion force between them. At pH 3 until 4, the result showed a drastic increase for adsorption of lead ions.

According to Kumar and Bandyopadhyay (2008), another term in describing the drastic increase in adsorption capacity was also known as pH adsorption edge thus in this work pH adsorption edge can be noted at pH range from 3 until 4.The maximum uptake of lead (II) ions occurred at pH 5 with 6.191 mg g-1. This can be clarified by noting that when pH of the solution was changed to a higher pH value, it reduces the amount of hydrogen ions thus providing more binding sites for attachment of lead ions. In addition, as pH increases deprotonation take place and negative charge of adsorbent was increased.However, as pH value beyond pH 6, the precipitation of ions may occur because of the solution contain higher amount of hydroxide ions (Witek Krowiak et al., 2011). Same observation have been reported from the previous study on removal lead (II) ions by different waste materials (Abdulrasaq & Basiru, 2010; Olu-Owolabi et al., 2012). Consequently, more positively charged of lead ions were attracted to the surface of CCX thus enhance the adsorption capacity.

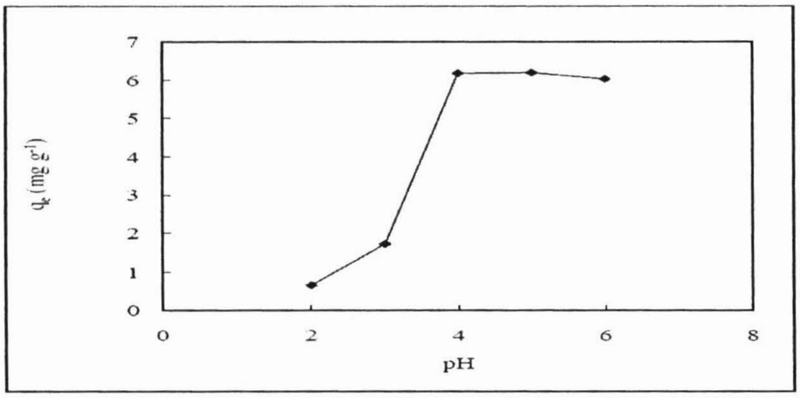

Figure 4.2 Effect of pH on the removal of lead (II) ions onto CCX.

Effect of adsorbent dosage

The result on the study of adsorbent dosage in removing lead (II) ions from the aqueous solution is presented in Figure 4.3. From the figure it clearly stated that as the amount of adsorbent dosage increase significantly from 0.02 g up to 0.08 4, percent removal of lead (II) ions also increased. However, percent removal of lead (II) ions remains constant when the adsorbent dosage increases from 0.04g to 0.10 g. This result explained that, when the adsorbent dosage was raised, the percentages adsorption generally increases because greater surface area of the active sites provided which allow the metal ions to penetrate easily on the adsorption sites. Furthermore, the presence of the functional groups on the CCX also could be associated with the penetration of the metal ions (Venkata et al., 2012). Besides, this result suggests that 0.08 g of adsorbent dosage is good enough to reach the adsorption equilibrium. However, percent removal slightly decrease as amount of adsorbent dosage is beyond than 0.08 g and this may be due to insufficient sites for the available lead (II) ions to cover all the exchangeable binding sites on the surface of adsorbent (Torab-Mostaedi et al., 2013). On the other hand, the amount of adsorption capacity decreased with the increase in the adsorbent dosage mainly due to the aggregation between adsorbent thus making the amount of surface areaof adsorbent reduced and blocked some of the binding sites (Ibrahim et al., 2010).

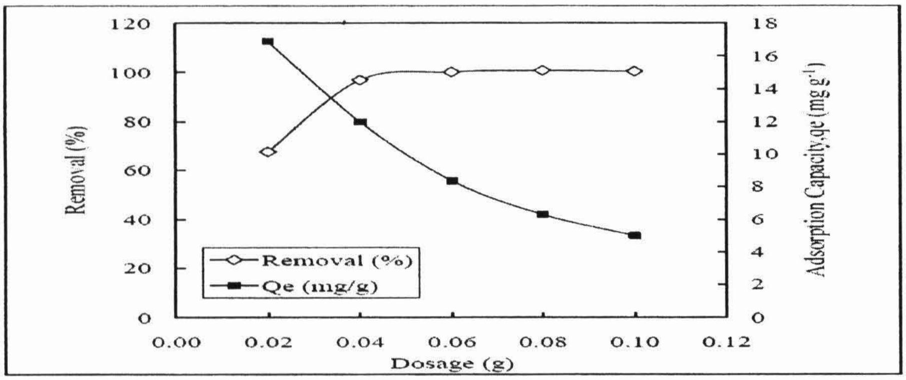

Figure 4.3 Effect of adsorbent dosage on the removal lead (II) ions onto CCX.

Adsorption kinetics studies

The adsorption kinetics was investigated for a better understanding on the reaction pathways between the adsorbent and adsorbate as well as the time needed in order to attain the adsorption equilibrium. The dependent mechanisms of the adsorption processes such as mass transfer, film diffusion, pore diffusion, and chemical reaction was studied by kinetic models (Ofomaja et al., 2008; Fonseca-Correa et al., 2013). In other word, by applying this kinetics studies, both physical and chemical characteristics of adsorbent could be examined. The two common models which have been widely used in order to study the rate of adsorption capacity of lead (II) ions onto CCX powder were pseudo first order and pseudo second kinetic models. The correlation coefficient (R2) obtained from the plots and intercept in both model were used to evaluate the efficiency of the adsorption for conformity between calculated and experimental predicted values.

Table 4.5 Pseudo-first-order and pseudo-second-order models for adsorption of lead (II) ions onto CCX.

Initial lead ion concentration (mg L^{-1})		**Pseudo-first-order**			**Pseudo-second-order**		
	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	K_2 (min $^{-1}$)	R^2
10	6.214	74.37	0.0032	0.8886	6.281	0.087	0.9977
20	12.205	66.29	0.0025	0.8982	12.239	0.029	0.9968
30	16.504	51.24	0.0012	0.7052	16.077	0.023	0.9983

From table 4.5, the pseudo-first-order and pseudo-second-order plot obtained, the correlation coefficients, R2 were higher than those pseudo-first-order with R2 value almost to unity and the calculated adsorption capacity (qe,cal) was very close to the experimental adsorption capacities (qe,exp). Therefore, amount of lead (II) ions adsorbed onto CCX followed well pseudo-second-order kinetic model thus strongly supports an assumption that the uptake process of lead (II) ions onto CCX was dominated by chemisorptions. It was observed that, increasing in lead (II) ions concentration would cause the rate constant of pseudo-second-order decreased. This condition could be explained by increasing more lead (II) ions concentration in solution, the harder lead (II) ions compete for the adsorption sites

Adsorption isotherm

Isotherm study was used to understand further the concept of adsorption process. Adsorption isotherm indicates the relationship between the adsorbate concentration in bulk and the adsorbed amount per unit weight of adsorbent (qe mg g-1). The adsorption isotherm also can be described through a curve associating the solute concentration in solution and the solute concentration at equilibrium on the surface of an adsorbent. Isotherm study proposed an assumption that adsorption site is equivalent and provide information on adsorption mechanisms. The data obtained from the adsorption experiments are applied into two famous models, Langmuir and Freundlich models for a better understanding the interaction between the adsorbate and adsorbent.

Table 4.6 Langmuir and Freundlich isotherm constants with correlation coefficients for the removal of lead (II) ions by using treated corncob.

	Langmuir			**Freundlich**		
	q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	K_F	n	R^2
Pb(II)	16.39	2.90	0.999	10.30	3.80	0.964

The values of R2 for Langmuir model showed much better as compared to Freundlich model. This indicates that, adsorption of lead (II) ions was fittedwell with Langmuir model. Tan et al. (2010) also reported that Langmuir model interpreted well the data for the adsorption of lead (II) ions onto modified and native corncobs. The maximum adsorption capacities of lead (II) ions are calculated and the value was recorded as 16.39 mg g-1. This value obtained may due to the xanthation process. Xanthation process caused the presence of sulphur atom in CCX which may enhance the adsorption capacity of lead (II) ions. The lone pair of electrons of sulphur atom is bound to an empty orbital of lead (II) ions forming stable complexes thus resulting in high uptake efficiency. Compared to the other adsorbents that have been used as summarized in Table 4.7, it was found that qmax values obtained is comparable.

Table 4.7 Comparisons of highest adsorption capacities for removal of lead (II) ions by various adsorbents.

Adsorbent	q_{max} **(mg g^{-1})**	**Reference**
Soda lignin	46.72	Ibrahim *et al.* 2010
Tobacco dust	39.60	Qi and Aldrich 2008
Agave bagasse	36.00	Velazquez-Jimenez *et al.* 2013
Eggshell	22.90	Ahmad *et al.* 2012
Pigeon peas hulls	20.83	Venkata Ramana *et al.* 2012
Corncob	16.39	This study
Heartwood of *Areca catechu*	11.72	Chakravarty *et al.* 2010
Maize husk	9.33	Adeogun *et al.* 2012
Almond shell	8.08	Pehlivan *et al.* 2009
Sugarcane bagasse	7.29	Martin-Lara *et al.* 2010
Rice husk	5.69	Zulkali *et al.* 2006

Conclusion and recommendations

This study identified the feasibility of corn cob waste which are abundant in nature and low cost as an adsorbent in order to immobilize lead (II) ions from aqueous solution. FTIR spectra analysis infers the functional groups that are responsible in adsorption of heavy metals were hydroxyl and carbonyl groups. Corncobs which have been modified chemically in alkali treatment with carbon disulfide CS2 have enhanced the adsorption efficiency for lead (II) due to the presence of a new sulphur groups. The alkalization process involved generation new active sites and permits the attachment of the metal ions. The parameters that have been implied in order to study the adsorption capacity were pH, CCX adsorbent dosage, initial concentration and contact time, kinetic study, and isotherm study. The result showed that, as the pH solution increased, the uptake of metal ions also increased and the desired value of pH was at pH 5.

From the kinetic data, it was found that at 120 min the equilibrium was achieved and pseudo-second order model was better fitted than pseudo-first order model as the correlation coefficient, R2 obtainedlies between 0.9968 – 0.9983. The Freundlich and Langmuir adsorption model have been applied and the result indicates that this adsorption study obeyed the Langmuir adsorption model as the maximum uptakes capacity of lead (II) ions by treated corncob (CCX) was 16.39 mg g-1. The possible mechanisms involved a monolayer process which lead (II) ions only attach on the outer surface of corncob. Therefore, this presence study suggest that corncob waste have a potential as adsorbent in order to treat the aqueous solution containing lead (II) ions since corncob are locally available in natural and relatively low cost.

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