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Study of lead ion elimination from aqueous solution in a fixed-bed double column system using longan seed based activated carbon

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Longan seed based activated carbon has been used for the adsorption of lead ions from aqueous solution in a fixed-bed double column set up. The effects of initial concentration of lead ion (20, 30, 40, and 50 ppm) and initial solution pH (4, 7, and 9) were studied to determine the maximum uptake of lead ion at room temperature. It was observed that the adsorption of lead ions onto activated carbon depends on initial pH and initial concentration of lead ions. The optimal value of pH was established as 7. A breakthrough period of approximately 9 h was established for continuous adsorption of lead from a 40 ppm solution at pH 4. The lead ion concentrations in the effluents were below 0.05 ppm during the first 7 h of adsorption.

Keywords: Fixed-bed column, longan seed, activated carbon, lead ion adsorption, water purification

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1. Introduction : The excessive release of heavy metals into the environment is a major concern worldwide [1]. Furthermore, heavy metal ion contamination of drinking water and wastewater is a serious and persistent problem [2]. Adsorption process is among the most effective techniques for heavy metals removal from waste streams [3]. Removal of metal ions from aqueous solutions by adsorption on abundant and low-cost adsorbents is one of the possibilities [4]. Generally wastewater treatment requires the use of highly effective and environmentally friendly techniques. Various technologies and techniques are available for water treatment including the use of activated carbon [5]. Activated carbon is the most widely used adsorbent for wastewater treatment and water pollution control. It is assumed that the metal ion removal by activated carbon takes place through a surface complex formation [6]. The ability of activated carbon to remove metal ions from solution depends on the textural properties of the activated carbon, including total surface area and pore size, and its surface chemistry based on heteroatom concentrations. The surface chemistry can be inferred from carbon pH [7]. The activated carbons prepared from lignocellulosic materials are good absorbents. These materials have been prepared from coconut shell [8], coffee residue [9], apple pulp [10], tamarind wood [4, 11], hazelnut husks [12], cones of the *European Black* pine [13], palm shell [14], and longan seed [15].

The removal of heavy metals using adsorbents can be done in batch or fixed-bed column set ups. The batch adsorption technique using activated carbon has been studied by Depci et al. [10], Acharya et al. [4], Singh et al. [11], Imamoglu & Tekir [12], Momčilović et al. [13], Xu & Liu [2], Li et al. [16], Rao et al. [17], Mohammadi et al. [18], Sekar et al. [8], and Boudrahem et al. [9]. On the other hand, the continuous-flow column operation for metals removal has been studied by Goel et al. [19], Sulaymon, et al. [20], Issabayeva et al. [14], and Chen and Wang [6]. The batch adsorption technique is not suitable for large size water treatment or drinking water production. The fixed-bed column set up usually consists of one column suitable for short time applications.

In this research, the continuous adsorption of lead in a two fixed-bed column set up loaded with longan seed based activated carbon bed was studied. The effects of initial concentration of lead ions (20, 30, 40, and 50 ppm) and solution pH (4, 7, and 9) were studied to determine the maximum uptake of lead ion at room temperature. The purpose of this experiment is to increase the duration of the water filter for drinking water production.

2. Materials and methods

2.1 Longan seed based activated carbon: Longan seed based activated carbon produced at the Department of Chemistry, Faculty of Science, Naresuan University, Thailand, was used as adsorbent for lead ion adsorption. This activated carbon was activated with 85 % H_3PO_4 using a weight to volume ratio of logan seed: H_3PO_4 1:0.5 and carbonized at 500 $^{\circ}$C [15]. The longan seed based activated carbon was ground, sieved (60 mesh) (Laboratory test sieve, Retsch, Germany), washed with distilled water, and then dried in an oven (SL shellab, 1350 FX, USA) at 105 ^{o}C for 3 h. The commercial activated carbon was obtained from market in Phitsanulok, Thailand.

2.2 Lead ion solution: A 1000 ppm solution of lead (AAS grade) was used as a stock solution. The stock solution was diluted with distilled water to 20, 30, 40 and 50 ppm. The pH of the lead solutions at each concentration was adjusted to 4, 7, or 9 using 0.1 M HCl (J.T.Jaker, USA) or 0.1 M NaOH (Merck, Germany). The pH values of the prepared solutions were measured by a pH meter (HORIBA F-21, Japan). The lead solution of different concentrations and pH were filled into 50 L plastic tank.

2.3 Fixed-bed double column set up: The experimental arrangement is shown in Figure (1). The system consists of two columns made from PVC tubes with 55 mm diameter and 600 mm height (number 1 and 2 in Figure 1). The columns were mounted vertically. The columns were packed with 600 g longan seed based activated carbon or commercial activated carbon, which filled the columns to the height of 450 mm. The two fixed bed column set up was used to simulate the removal of lead ions from aqueous solution in a continuous manner using a filtration process. The lead ion aqueous solutions having different concentration and pH were fed into the activated carbon columns from a 50 L plastic tank positioned above the top of the columns. The flow rate used was 3 L/h. The control valves to regulate the flow rate are incorporated into the feed line of the columns. Samples of the solutions were collected after passing both columns. The residual concentrations of lead in effluent solutions were determined using atomic adsorption spectrophotometer (Varian SpectrAA 220, Australia).

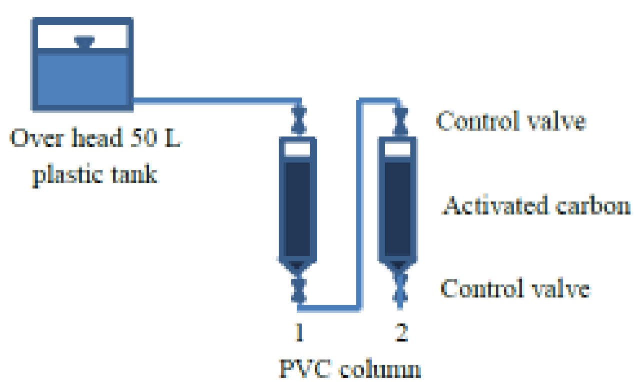

Figure (1): The schematic diagram of fixed-bed double column set up used in this work.

2.4 Breakthrough experiment

The 40 ppm and pH 7 lead solution was selected to be used for the breakthrough experiment. The experiment was conducted with a flow rate of 3 L/h using the column set up packed with both the longan seed based activated carbon or commercial activated carbon. Samples of the efflux were collected every 30 minutes and their lead content was measured. The breakthrough point is defined as the time point when the analyte concentration in the effluent (C_{eff}) reaches approximately 3 – 5 % of the influent analyte concentration (C_{inf}) **[21]**. Breakthrough curves were plotted using ratio of effluent and influent concentrations (C_{eff}/C_{inf}) versus time (h) **[22]**.

3. Results and discussion

3.1 The effect of initial pH of lead ion solution: Lead concentrations of effluents resulting from solutions with different initial pH and lead ion concentration are shown in Table (1). The results indicate that the removal of lead ions using activated carbon depends on initial pH and initial lead concentration of lead. It was also shown that the lead concentration of effluent from the solution with initial pH 4 is relatively higher than at pH 9. Lowest lead concentrations in the effluent were obtained at pH 7 for all of the initial lead concentrations. This result is valid for both types of activated carbon used. It needs to be stressed that seven lead species, such as Pb^{2+}, $Pb(OH)^{+}$, $Pb(OH)_2$, $Pb(OH)_3^{-}$, $Pb(OH)_4^{2-}$, $Pb_2(OH)^{3+}$ and $Pb_3(OH)_4^{2+}$, can be present in aqueous solution depending on pH. Pb(II) predominantly appears as Pb^{2+} at pH < 6 **[23]**. It is assumed that the lead ion removal by activated carbon materials happens according to the surface complex formation models exemplified by the following equation; $Pb^{2+} + SOH \rightarrow SOPb^{+} + H^{+}$, where SOH represents the surface functional group of activated carbon responsible for lead adsorption. As pH is increased or concentration of hydrogen ions is decreased, the reaction is shifted from left to right, which results in the formation of higher density of surface complexes ($SOPb^{+}$) and higher level of lead removal **[6]**. At pH 4.0, Pb^{2+} is the main lead species in aqueous solution. The low lead ion adsorption at pH 4 could be ascribed to the diminshed electrostatic attraction between Pb^{2+} cations and the protonated surfaces of the activated carbons as well as to the competition between Pb^{2+} and H^{+} for these sites. The acidic groups on surface of activated carbons are in their protonated forms at pH 4. Therefore, the uptake of Pb(II) difficulties hindered due to diminished electrostatic attraction. Simultaneously, the excess of H^{+} ions in bulk solution can compete with Pb^{2+} and result in a low Pb(II) uptake **[23]**. However, it was suggested that lead adsorption does occur, albeit to a small extent, at pH 4. This suggests that apart from electrosorption, lead retention on activated carbons may occur by other mechanisms such as ion exchange **[7]**.

Table 1 The lead ion concentration of effluents at different pH and lead concentration values.

Initial pH	Lead ion concentration of effluents after adsorption by activated carbon							
	Longan seed based activated carbon				Commercial activated carbon			
	Initial lead ion concentration				Initial lead ion concentration			
	20 ppm	30 ppm	40 ppm	50 ppm	20 ppm	30 ppm	40 ppm	50 ppm
4	0.18	0.26	0.35	0.37	1.78	1.92	1.56	2.59
7	0.00	0.02	0.04	0.18	0.00	0.65	0.78	0.98
9	0.15	0.18	0.26	0.31	0.65	0.92	1.06	1.27

Lead adsorption is maximal at initial pH of 7 for all initial lead concentrations and using both types of activated carbons. This result is in agreement with the study of Imamoglu and Tekir **[12]**. Thus the effluent at pH 7 contains lower lead concentration than at pH 4 or 9. It was discovered that the negative charge density on the activated carbon surface is a high at pH 7 due to deprotonation of the lead binding sites **[24]**. At pH 9 (i.e. alkaline solution) the adsorption of lead ion is higher than at pH 4. The high extent of lead removal observed at pH 9 is due to lead hydrolysis and precipitation of $Pb(OH)_2$ **[9-**

10,13];. It is associated with decreased competition between protons and lead ions for adsorption sites on the carbon surface [14]. The precipitated $Pb(OH)_2$ is also partially filtrated by the activated carbon.

3.2 The effect of initial concentration of lead ion solution: The lead concentrations in the effluents increased with increasing initial lead concentrations for all initial pH values. This result is in accord with the work of Imamoglu and Tekir [12] who demonstrated that there are sufficient adsorption sites to efficiently adsorb lead at lower initial concentration, however, at higher lead concentration the number of adsorption sites is insufficient for efficient lead adsorption. The adsorption of lead ion of longan seed based activated carbon is more efficient than on commercial activated carbon for all condition. The results indicate that activated carbon produced from longan seed residue with H_3PO_4 activation is an effective adsorbent for the removal of lead from aqueous solutions.

3.3 The result of breakthrough experiment: Initial experiments have shown high efficiency of lead adsorption from solutions at pH 7 containing lead at 40 ppm concentration. These conditions were therefore selected for the breakthrough experiment. The breakthrough curves for both activated carbons are shown in Figure (2). Both breakthrough curves are S-shaped and are similar to results obtained with granular activated carbon in fixed-bed set up [20, 22] and activated sludge in fixed bed adsorber [25]. It was established that the fixed bed double column set up packed with longan seed based activated carbon is suitable for the adsorption of smaller molecular weight molecules with simple structures [21].

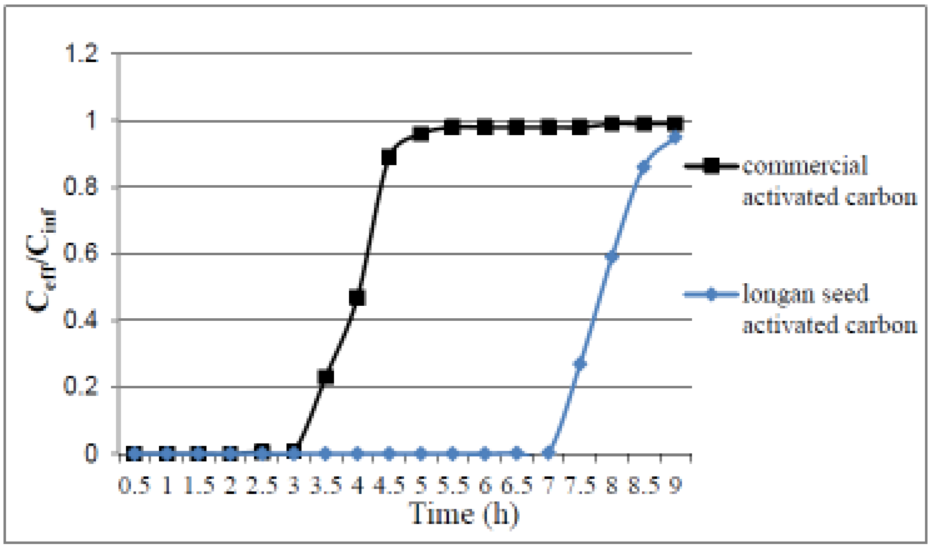

Figure (2): The breakthrough curves for pH 7 and 40 ppm lead solution passed through activated carbons.

Continuous adsorption of lead showed that the breakthrough period for commercial activated carbon (4.5 h) was shorter than the longan seed based activated carbon (9 h). The experimental results demonstrated that a fixed bed double column set up packed with longan seed based activated carbon can be successfully used to remove lead from aqueous solution. It is interesting to note that the lead ion concentration of effluent obtained from this set up remained below maximum allowable lead concentration in drinking water (0.05 ppm), which has been set by the US Environmental Protection Agency [7], until 7 h of flow time. This is longer than for a column packed with the palm shell activated carbon (about 2.5 h) [14], granular activated carbon in fixed-bed adsorber (about 3 h) [20], and activated sludge in fixed bed adsorber (about 7 h) [25].

4. Conclusions: Continuous adsorption of lead ions in fixed-bed double column set up packed with longan seed based activated carbon has indicated that the removal of lead by activated carbon materials depends on initial pH and initial lead concentration. It was also shown that the lead concentration in effluents for samples with pH 4 is higher than at pH 9. Lead concentration in the effluent was lowest for all initial lead concentrations at pH 7. The breakthrough period in a fixed-bed double column set up packed with longan seed based activated carbon for a 40 ppm and pH 7 lead solution is 9 h. The lead concentration in the effluent remained below the maximum allowable lead concentration in drinking water, set by the US Environmental Protection Agency, until 7 h of flow time. The results of this study show that continuous adsorption of lead in a fixed bed double column set up packed with longan seed based activated carbon can be sufficiently efficient for lead removal from aqueous solutions.

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