

Removal of Pb(II) from Aqueous Solutions Using Mixtures of Bamboo Biochar and Calcium Sulphate, and Hydroxyapatite and Calcium Sulphate

Ahmed Hassan and Lupong Kaewsichan

Department of Chemical Engineering, Prince of Songkla University, Hat Yai, Songkhla, Thailand

Abstract

Sorption characteristics of Pb(II) from aqueous solutions through a low-cost adsorbent mixture comprising of Bamboo biochar (BB) and Calcium Sulphate (CS), and a more expensive mixture of Hydroxyapatite (HAP) and Calcium Sulphate (CS), were investigated. The effects of equilibrium contact time, and adsorbate concentration conducted in batch experiments were studied. Adsorption equilibrium was established in 40 (min). The adsorption mechanism of Pb(II) from these two adsorbent mixtures was carried out through a kinetic rate order. A pseudo second-order kinetic model was applied for the adsorption processes. The model yielded good correlation ($R^2 > 0.999$) of the experimental data. Adsorption of Pb(II) using (BB&CS) and (HAP&CS) correlated well ($R^2 > 0.99$) with both the Langmuir and Freundlich isotherm equations under the concentration range studied. Hence, the effectiveness of an inexpensive natural material (BB&CS) mixture in Pb(II) removal is established, and is promising for use in other heavy metal adsorptions.

Keywords: natural adsorbents; bamboo biochar; calcium sulphate; hydroxyapatite; heavy metal adsorption

1. Introduction

Heavy metals generally are recognized to be a threat toward humans and ecosystems because of their high toxicity (Ramesh *et al.*, 2013). Contamination from them has attracted considerably global attention, according to their voluminous discharge into the environment from industrial activities (Heidari *et al.*, 2013). Lead is a toxic element for humans and animals at some concentration and a serious public health issue worldwide (Xu *et al.*, 2007). Lead as the form of Pb(II) is often found in textile dyeing, ceramic and glass industries, petroleum refining, battery manufacture and mining operations (Freitas *et al.*, 2008). It is extremely toxic and can damage the kidney, liver, brain, nervous, and reproductive systems (Ramesh *et al.*, 2013); among other adverse effects to humans (Godwin, 2001). Therefore, it is necessary to eliminate such hazardous heavy metal ion in wastewater before discharging it into the ecosystem (Farghali *et al.*, 2013). Subsequently, considerable efforts have been spent in treating Pb-containing wastes at their source.

Traditional techniques for the elimination of heavy metal ions include precipitation, membrane filtration, sorption, and ion exchange, etc. (Zhao *et al.*, 2011; Matlock *et al.*, 2002; Yang *et al.*, 2011). For all treatment methods, it is a struggle between cost-effectiveness and environmental regulations. One of these methods, the sorption technique, has been used widely because it

is simple, economical, and cost-effective (Zhao *et al.*, 2011). In this method, material like biochar has been used as adsorbent. It has shown strong sorption affinity for organic compounds and may play an important role in controlling organic pollutants in the environment (Cornelissen *et al.*, 2005). Main benefit for the use of biochar is from its structured carbon matrix with high degree of porosity and extensive surface area that enhances its sorbent characteristics, thereby plays an important role in controlling contaminants (Chen *et al.*, 2011). Wood biochar, especially bamboo biochar (BB), has higher carbon content and is more hydrophobic and aromatic than those produced from rice husks, moreover, bamboo biochar is a material with the lowest level of humification (Zhang *et al.*, 2014) suitable for removal of metal ions. Its high sorption is due to three mechanisms: electrostatic interactions; ionic exchange between ionisable protons and heavy metal cations; and sorptive interaction (Xu *et al.*, 2013). Furthermore, the mechanism of biochar adsorption depends on functional groups, specific surface area and many other parameters (Kołodźńska *et al.*, 2012).

Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; HAP] is the main mineral constituent of teeth, bones and phosphate mineral rocks (Zamani *et al.*, 2013). Many research works have found that (HAP) can effectively remove lead ion in aqueous solution under different experimental conditions and show potential removal capacities, with removal percentage trending to 100% (Xu *et al.*,

2007). Synthetic hydroxyapatite (HAP) has been extensively studied for its kinetics and chemical reaction with a wide variety of metals e.g., Pb, Cu, Cd, Zn, Sb and U (Liao *et al.*, 2010; Corami *et al.*, 2007; Peld *et al.*, 2004; Leyva *et al.*, 2001; Fuller *et al.*, 2002). Many types of reaction control Pb removal by (HAP) and other adsorbents, including surface adsorption, cation substitution or precipitation. Using (HAP), adsorption of Pb ions on the surfaces of the adsorbent will be followed by ion exchange reaction amidst the Pb(II) adsorbed and the Ca⁺² ions in (HAP) (Takeuchi and Arai, 1990).

Calcium salts (chlorides, sulphates, and carbonates) are better lead precipitators than the corresponding sodium salts (Agwaramgbo *et al.*, 2013). Moreover such composites have been described for use as resorbable biomaterials in bone surgery (Evaniew *et al.*, 2013), but have never been used for the retention of heavy metals from polluted water (Belaicha *et al.*, 2014). The present work aims to investigate and compare two adsorbent mixtures; (BB&CS), and (HAP&CS), in the study of Pb(II) ions removal from aqueous solutions which involves equilibrium contact time, adsorbate concentration, adsorbent dose, their kinetics through pseudo second-order and applicable to the two isotherm models.

2. Materials and Methods

2.1. Materials

The (BB) used in this study was prepared in the laboratory by pyrolysis process at 500°C; (HAP) was a commercial type purchased from Sigma-Aldrich (Thailand) Co. LLC; and (CS) was bought from Aldrich Chemicals and was used without further purification. Pb(NO₃)₂ (Lead Nitrate) standard samples were acquired from Boss Official Limited Partnership in Thailand.

2.2. Method

2.2.1. Properties of biochar

Fourier transforms infrared spectroscopies (FTIR) (Bomem, MB 100) were carried out to identify the functional groups of the biochar. Scanning electron microscopy (Hitachi JSM-6700F SEM) was implemented to observe the surface microstructures of the biochar. The pH of the (BB) was measured by suspending the (BB) with demineralized water at a mass ratio of 1:20. The solution was then hand-stirred and allowed to stand for 5 (min) before measurement

with a pH meter (Inyang *et al.*, 2012). The (BB) surface potential was determined by measuring the zeta potential (ζ) of the colloidal biochar suspension obtained through sonication according to the procedure of Johnson *et al.* (1996). Charge mobility of each suspension was determined using Brookhaven Zeta Plus (Brookhaven Instruments, Holtsville, USA), and Smoluchowski's formula was used to convert the electric mobility into zeta potential.

2.2.2. Preparation of metal solutions

All metal solutions were prepared from their nitrate salts (Analytical Reagents; AR) and distilled water. The synthetic solutions were all prepared by diluting Pb(II) standard stock solutions (concentration 1000 ± 2 (mg/L)) obtained by dissolving appropriate amounts of metal salt in double distilled water. Four dilutions: 100, 200, 300 and 400 (mg/L), were used in each set of the experiment.

2.2.3. Sorption studies

Batch adsorption experiments were conducted on the three adsorbent materials, for which 0.08 (g), 0.05 (g), and 0.05 (g) for (BB), (CS) and (HAP), respectively, were used to produce the two mixtures. Each mixture of (BB&CS) and (HAP&CS) was put into a 250 (mL) conical flask containing 50 (mL) of Pb(II) ions at the pre-set concentrations mentioned earlier of 100, 200, 300 and 400 (mg/L), shaken, filtered and subjected to Pb(II) analysis to determine the optimum Pb(II) adsorptions. The effect of contact time was studied in the time range of 0-40 (min). At the end of the adsorption process the suspensions were filtered through 0.45 (μm) syringe membrane filters and the corresponding supernatant was analysed employing a Perkin Elmer Thermos Scientific S-series model (AAAnalyst100) Flame atomic absorption spectrophotometer (AAS) for residual Pb(II) concentrations. Three replicates were conducted for each Pb(II) bio sorption experiment set, and the average values determined. The adsorbent capacity of (BB&CS) and (HAP&CS) mixtures were calculated using general equation (1), (Tangjuank *et al.*, 2009):

$$q_e = (C_0 - C_t) \frac{V}{M} \quad (1)$$

Where q_e is the amount of Pb(II) adsorbed on the adsorbent (mg/g); C_0 and C_t are the Pb(II) concentrations in the solution before and after adsorption (mg/L); V is the volume of the solution (L); and M is the amount of the adsorbents used in the reaction mixture (g).

2.2.4. Adsorption kinetics

The mechanism of sorption can be explained by the kinetic characteristics of sorption. For this purpose, pseudo second-order kinetic model was considered and fitted with the experimental data. The pseudo second-order reaction rate equation, as shown by (Ho *et al.*, 1999), is described in equation (2):

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (2)$$

Where q_t is the amount of metal ions adsorbed (mg/g) at any given time t (min); q_e the amount of metal ion adsorbed (mg/g) at equilibrium; and k_2 the second-order reaction rate constant for adsorption (g/mg min). Though there is a high possibility for pore diffusion to be the rate limiting step in the batch process, the adsorption rate parameter, which controls the batch process for most of the contact time, is the inter-particle diffusion (Ramesh *et al.*, 2013; Weber and Morris, 1963; Allen *et al.*, 1989)

2.2.5. Adsorption isotherms

Equilibrium isotherms were described by the sorption. Adsorption of Pb(II) by (BB&CS) and (HAP&CS) were studied further to understand the mechanism by fitting the experimental data to Langmuir and Freundlich adsorption isotherms. The Langmuir isotherm assumes monolayer adsorption onto a surface with a finite number of identical sites, and its linear form is expressed in equation (3), (Kołodziejńska *et al.*, 2012):

$$\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}} \quad (3)$$

Where q_e and q_{max} are the observed and the maximum uptake capacities (mg/g); C_e the equilibrium concentration (mg/L); and b the equilibrium constant (L/mg). The degree of suitability R_L was estimated from the value of separation factor, which can be obtained by equation (4), as shown by (Weber and Chakravorti, 1974):

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

The Freundlich equation proposes an empirical model based on the sorption on heterogeneous surface, and is in the form of equation (5), (Kołodziejńska *et al.*, 2012):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

Where K_f (L/g) and n are the Freundlich isotherm constants and intensity of adsorption, respectively; q_e and C_e are as described for equation (3).

3. Results and Discussion

3.1. Characteristics of biochar

FTIR analysis of the (BB) revealed many functional groups on the (BB) surfaces: the bands assigned to O-H stretching; aliphatic C-H stretching; C-H stretching bands associated with aliphatic functional groups; intense bands of aliphatic CH₂; intensity of aromatic C=C stretching and C=O stretching of conjugated ketones and quinones; C=C ring stretching vibration of lignin; aromatic C=C stretching (out of plane deformation by aromatic C-H groups and could have been caused by carbonates); and C-O and C-C stretching. The (BB) characteristics shown by SEM on morphology are large internal surface and porous structure with an approximate porous space of 38.67 (μm). SEM on elemental composition in the (BB) samples showed available C, S, K, Cl elemental percent contents of 58.61, 1.55, 30.46, and 9.38, respectively. Physicochemical properties of (BB), like pH, zeta potential for surface, and surface area available, are important factors controlling their environmental applications (Inyang *et al.*, 2010). In this study, zeta potential for surface measurements indicated that the (BB) had more negative surface charge, which may be related to the surface area and the pore volume. This data seemed to predict a greater potential to adsorb abundant positively charged heavy metals and confirmed the SEM results. The zeta potential data values for (BB), (HAP&BB&CS) mixture and (HAP&BB) mixture were -56, -2, and -19 (mV), respectively.

3.2. Effect of contact time

Adsorption characteristics can be explained by the effect of contact time. Fig. 1 showed the effect of contact time between the solution containing Pb(II) and mixture adsorbents from two combinations of (BB&CS) and (HAP&CS) that were contacting inside the shaken conical flask. The four concentrations used were in the range of 100 to 400 (mg/L) and the adsorption contact times were operated up to 40 (min). The percentage of adsorbed Pb(II) with different contact time was shown in the figure. It can be observed that the rate of Pb(II) ions removal was higher at the incipient step through

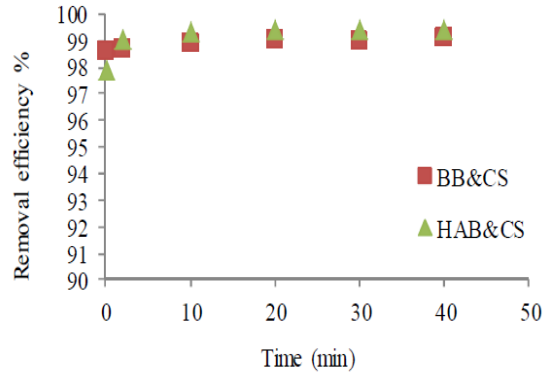


Figure 1. Pb(II) removal efficiency vs. contact time for the (BB&CS) and the (HAP&CS) adsorbent mixtures

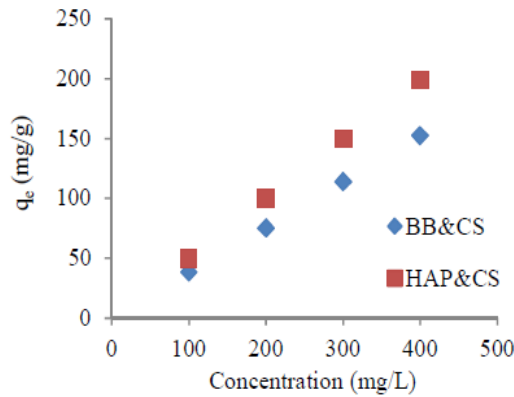


Figure 2. Effect of initial Pb(II) concentration C_e on the equilibrium capacity q_e for the (BB&CS) and the (HAP&CS) adsorbent mixtures

accessibility of additional energetic scenes on the surface of both adsorbents, after that it became slower at subsequent period of contact time through shorter or fewer number of energetic scenes. Clearly from the figure, the percentage of Pb(II) removal from the aqueous solution increased rapidly and reached up to 99% at 40 (min). Augment of impinge time had a measly impression on the percentage of removal, and 40 (min) shaking time was thus adopted as an equilibrium time for maximum adsorption. The rate of Pb(II) removal that decreases with time may be due to aggregation of Pb(II) around (BB) and (HAP) particles in the adsorbent mixtures. This aggregation hinders the migration of adsorbate, as the adsorption sites become filled up, and that the resistance to diffusion of Pb(II) molecules in the adsorbents increases (Mittal *et al.*, 2010). Equilibrium time for both adsorbents was reached in less than 40 (min), meaning that both adsorbents had similar behaviour to adsorb Pb(II).

3.3. Effect of initial metal ion concentration

As stated earlier, the experiments were carried out for four discrete concentrations of Pb(II) solution (100, 200, 300 and 400 (mg/L)). The effect was investigated and presented in Fig. 2. The adsorption capacity of Pb(II) by the adsorbents, (BB&CS) and (HAP&CS), increased with increasing initial concentration of metal ion for both mixtures. The maximum equilibrium uptake for Pb(II) were found to be 152.4 (mg Pb(II)/g) for the (BB&CS) mixture, and 200 (mg Pb(II)/g) for the (HAP&CS) mixture. The adsorbent containing (BB) shown in Fig. 2, yielding low q_e is ascribed to a high contact probability between the (BB) and the lead ions. At low concentration level, lead ions were situated at the outer surface of the (BB) separately, however, with increasing solution concentration lead ions entered into the interior structure, resulting in higher removal capacity.

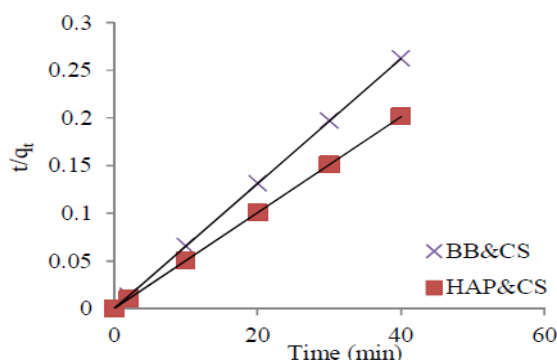


Figure 3. Removal capacity of Pb(II), pseudo second-order model fit, for (BB&CS) and (HAP&CS) mixtures

Table 1. Adsorption kinetic model rate constants for Pb(II) removal

Absorbent	q_{eExp} mg/g _{ad}	Langmuir		
		$q_e(cal)$ mg/g	k_2	R^2
BB&CS	152	151.5	0.73	0.99
HAP&CS	199	200	0.5	0.99

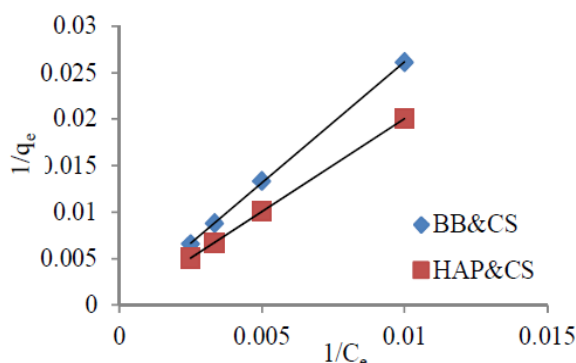


Figure 4. Langmuir isotherm $1/C_e$ vs. Pb(II) adsorption q_e for (BB&CS) and (HAP&CS) mixtures

Experimental and theoretically calculated adsorption capacities at equilibrium q_e , together with coefficients related to kinetic plots are listed in Table 1. Plotting the reaction rate t/q_t against time T , as shown in Fig. 3, was conducted for the initial Pb(II) concentration of 400 (mg/L) at room temperatures. The pseudo second-order adsorption rate constant k_2 and q_e were determined from the slope and the intercept of the plots.

It can be seen from Table 1 that linear correlation coefficients for the pseudo second-order kinetic model are good. Based on the comparison between experimental and theoretically calculated q_e values, it was also found that the model fitted well for removal of Pb(II) by both mixtures. The calculated (cal) values of q_e from the model provide a near-perfect match between the theoretical and the experimental q_e values, together with high correlation coefficients ($R^2 > 0.99$). The higher rate of metal adsorption for the (HAP&CS) mixture could be due to the presence of its more active sites, which were available in the adsorbents. The second-order

reaction rate constant, k_2 , for (HAP&CS) was found to be lower than that for (BB&CS). From the above discussion, pseudo second-order adsorption mechanism is predominant, meaning that chemical sorption takes part in the adsorption process. Once the sorptive sites are exhausted, the uptake rate is controlled by the rate of intra particle diffusion (Chaturvedi *et al.*, 2006). This model agrees with the assumption that the rate-limiting step is chemical sorption or chemisorption involving valence forces between adsorbent and adsorbate (Taty-Costodes *et al.*, 2003).

Fig. 4, using Langmuir model, and Fig. 5, using Freundlich model, show the intercept and slope for the straight lines used in the calculations of isotherm constants tabulated in Table 2. Langmuir is the more important model of monolayer adsorption, based on the assumption that there are a fixed number of adsorption sites, and each site can hold only one adsorbate molecule (the adsorbed layer is one molecule in thickness).

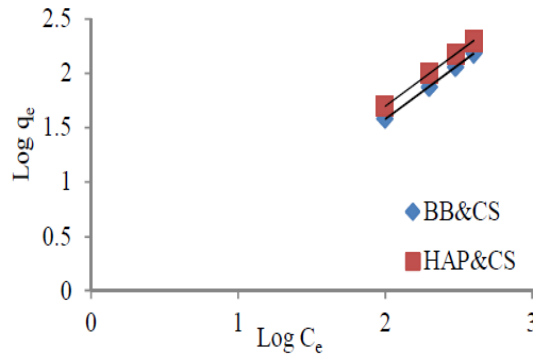


Figure 5. Freundlich isotherm $\text{Log } C_e$ vs. Pb(II) adsorption $\text{Log } q_e$ for (BB&CS) and (HAP&CS) mixtures

Table 2. Isotherm parameters for sorption of Pb(II) by different adsorbent

Absorbent	Langmuir			Freundlich		
	q_{\max}	b	R^2	k_f	n	R^2
BB&CS	152.4	0.0025	0.9998	0.387	1	0.998
HAP&CS	200	0.0025	0.99	0.51	1	0.99

Table 3. Ranges of R_L for type of Isotherm

Values of R_L	Type of Isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L < 0$	Irreversible

Table 3 shows the optimum range of the degree of suitability R_L . The value of R_L in the Langmuir model for the initial concentration of 400 (mg/L) was calculated to be 0.5, indicating that sorption of metal ions to (BB&CS) and (HAP&CS) adsorbents are optimum and the process is favourable.

The value n , equals 1 for both mixtures, also indicated that the Freundlich isotherm is acceptable (Farouq and Yousef, 2015). From Table 2 the coefficient of determination R^2 for the Langmuir isotherm is slightly better than that obtained from the Freundlich isotherm, and hence the Langmuir model is slightly more favourable. From the same Table, the removal capacity results q_{\max} showed that the removal efficiency using (HAP&CS) was definitely higher than when (BB&CS) was used. However, the lower-price (BB&CS) is still effective for Pb(II) removal; it could remove approx. three-fourths of the heavy metal comparing to the higher-price (HAP&CS), proving that adsorbent other than (HAP) can also yield adsorption favourable results. Moreover, the zeta potential charge of (BB), as evaluated and reported earlier on the (BB) char characteristics, is very low -56 (mV), indicating one more reason why it is effective.

4. Conclusions

Bamboo biochar (BB) and Hydroxyapatite (HAP) are capable of removing Pb(II) from aqueous solutions, particularly when they are mixed with Calcium sulphate (CS). Pseudo second-order model yielded very high regression coefficients, indicating excellent sorption of Pb(II) onto both mixtures. Pb(II) sorption using both adsorbents were fitted to the Langmuir and the Freundlich adsorption isotherms, and the Langmuir model had been found to be slightly more favourable. In our study, the adsorption capacities of the mix-adsorbents for a 400 (mg/L) Pb(II) contamination were found to be able to remove 152.4 (mg Pb(II) /g) when using (BB&CS), and 200 (mg Pb(II) /g) when using (HAP&CS). Though at three-fourths efficiency, this work has shown that low-cost (BB&CS) adsorbent can play an important role in adsorption of lead from water and/or wastewater, compared to the use of higher-price (HAP&CS). The combination of (BB) and (CS) to remove lead ions from aqueous solutions is found to be promising.

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Correspondence to

Mr. Ahmed Hassan Alamin
Department of Chemical Engineering,
Faculty of Engineering,
Prince of Songkla University,
Hat Yai, Songkhla 90112
Thailand
Email: ahmed.10000@yahoo.com