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Sorption of Pb Metal Using Bottom Ash as a Low Cost Sorbent

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Abstract: Recently, adsorption through the use of natural or recycled material is considered to be a low-cost alternative to remove heavy metals from wastewater. This study investigates the potential of coal bottom ash to be used as an adsorbent for the removal of lead (Pb) from aqueous solutions. The physical and chemical characteristics of bottom ash were determined and a series of batch leaching and adsorption experiments were performed to determine efficiency of the adsorbent material. The adsorption capacity was determined as a function of the particle size, specific surface area and contact time. The rate of extent of adsorption is dependent on the specific surface area and particle size of the adsorbent wherein the adsorption rate increased as particle size decreased. Several kinetic models (Lagergren first-order, pseudo-second order and Elovich equation) as well as isotherm models (Langmuir and Freundlich) were applied to the experimental data. The pseudo-second order was found to be the most suitable model describing the adsorption of Pb. On the analysis of equilibrium isotherms, Langmuir isotherm was found to be the best representative for Pb-sorption on bottom ash.

Keywords: adsorption; bottom ash; isotherms; kinetics; leaching; lead

1. Introduction

The presence of heavy metals in the aquatic systems has been a major concern due to their toxic, cumulative and non-biodegradable characteristics. Lead (Pb) is considered to be one of the most toxic heavy metals that have been increasingly introduced into the natural waters. The permissible limit of lead in drinking water imposed by the Ministry of Environment in Korea is 0.05 mg/L [1]. Human exposure to Pb from different sources such as storage batteries, lead manufacturing and mining causes several illnesses such as anemia and hepatitis. Unlike most organic pollutants, heavy metals are generally refractory and difficult to detoxify biologically. Removal of heavy metals such as Pb is normally achieved by advanced technologies such as ion exchange, chemical precipitation, ultra-filtration, or electrochemical deposition [2]. However, application of such methods is sometimes restricted because of technical or economical constraints. Adsorption, on the other hand, is a most promising technique employing solid sorbents to remove toxic heavy metals from wastewaters. This process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pretreatment before its application.

Bottom ash is a voluminous solid waste by-product from coal-fired power plants. As of 2001, over 280,000 tons was generated in Korea. The increasing disposal of bottom ash poses a serious environmental problem and an alternate reutilization of the material has to be developed. Recently, there is a growing interest in bottom ash utilization, where it is used as a sorbent for various pollutants especially in water [3-5]. These research studies have investigated the possibility of using bottom ash as an adsorbent to remove various heavy metals from wastewater. The particle size, inherent large surface area and high porosity of bottom ash make it a good choice for use as a low-cost adsorbent.

The objective of this study was to assess the potential of coal bottom ash to adsorb Pb from aqueous solutions. The effect of bottom ash particle size and contact time on the removal of Pb was studied. Additionally, the leaching characteristics of bottom ash were investigated to evaluate whether this material is capable of releasing toxic heavy metals more than the Korean regulatory limit. Also, the kinetic and equilibrium isotherms of adsorption were established and modeled.

2. Materials and Methods

2.1. Experimental Materials

The bottom ash was obtained from a coal incinerator in Korea. It was sampled based on various sizes depending upon its physical and chemical composition and the incineration process. The samples were dried at 105°C for 10 hours and sieved to particle size classes of 4.75-

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2.00mm, 2.00-1.19mm and <1.19mm mesh in order to obtain a uniform size of the ash. The elemental com- position, surface area and mineral composition of bottom ash were analyzed using Scanning Electron Table 1. Surface area (m^2g^{-1}) and elemental composition (%) of bottom ash Microscopy-Energy Dispersive Spectroscope (SEM-EDS), BET surface area analyzer and X-ray diff- ractometer (XRD).

Particle size	Surface area	O	Si	Al	C	Mg	P	Fe	K	Na	Ca	Ti
<1.19 mm	8.47	64.19	16.16	6.18	4.93	2.85	2.10	1.47	1.15	0.78	0.14	0.02
1.19-2.00 mm	3.96	65.55	14.36	11.02	2.31	1.17	1.66	1.25	1.53	0.92	0.13	0.06
2.00-4.75 mm	1.41	68.97	14.54	6.24	3.85	0.63	2.34	0.87	1.34	0.81	0.30	0.09

Table 2. Heavy metal leached by KSLT.

Heavy metal	<1.19 mm	1.19-2.00 mm	2.00-4.75 mm	Limit
Cr	0.1124	0.1107	0.1106	0.5
Cu	0.0940	0.0910	0.0870	3.0
As	0.2978	0.2936	0.2900	1.5
Cd	0.1096	0.1097	0.1098	0.3
Hg	*nd*[a]	*nd*[a]	*nd*[a]	0.005
Pb	*nd*[a]	*nd*[a]	*nd*[a]	0.1

a. heavy metal not detected

2.2. Batch Leaching Test

Since bottom ash may contain potentially hazardous heavy metals, it is necessary to evaluate the possibility of leaching. The leachability of heavy metals from bottom ash was performed in accordance with Korean Standard Leaching Test (KSLT). Fifty grams of bottom ash samples were mixed with an extraction fluid (W:V ratio = 1:10) composed of 500 mL distilled water and HCl (pH = 5.8 – 6.3). The samples were shaken in a water bath shaker at the rate of 185 excursions per minute for 6.5 hrs at a constant temperature of 20°C. The leachate was vacuum filtered through a 1.0-μm filter paper and the concentrations of Pb, Cu, As, Hg, Cr and Cd in the supernatant liquid were then analyzed using an Inductively Coupled Plasma Atomic Emission (ICP-AES). If the amounts of heavy metals leached for the ash exceed the regulatory limits, the ash is classified as a hazardous waste.

2.3. Batch Adsorption Test

Batch adsorption experiments were carried out by using 100 g of bottom ash with 500 mL solution containing 10 ppm of Pb. The mixtures were vigorously shaken (100 rpm) in a water bath shaker at a constant temperature of 20°C. Small samples of the solution (≈20.0 mL) were taken out at a predetermined time intervals to measure the evolution of the adsorbate concentration. The samples were filtered through a 0.45-μm membrane to collect the supernatant and the residual metal concentration was determined using an ICP-AES.

3. Results and Discussion

3.1. Characterization of the Material

Table 1 summarizes the specific surface area and elemental atomic concentration of bottom ash. A material

is classified as homogeneous when the particle size has an effect on the amount of elements present in the material. The varying amounts of elements per particle size indicate that the material is heterogeneous. The main components detected by SEM-EDS were O, Si, Al and C with others found at low increase or decrease in particle sizes has concentrations. The results from XRD showed that the material has an amorphous nature indicated by the presence of quartz (SiO_2) and mullite ($Al_6Si_2O_{13}$). The presence of these minerals indicate that this bottom ash is aluminosilicate, a main mineral found in zeolite which is widely used as an adsorbent for the removal of the heavy metals [4].

3.2. Leaching Characteristics

A good adsorbent material is considered safe and efficient when it can effectively remove heavy metals without releasing potentially hazardous substances. Therefore, leaching tests were performed to evaluate the leachability of heavy metals from the bottom ash. Table 2 shows the leaching characteristics of heavy metals in bottom ash. During leaching tests, concentrations of less than 0.3 ppm were found for Cr, Cu, As and Cd, and no Hg and Pb metals were leached from the bottom ash, which passes the Korean regulatory limit. The release of heavy metals is limited since this material is amorphous in nature with little and no trace of heavy metals. The leachability of bottom ash was found to be dependent on the solubility of the heavy metal formed after incineration [4]. It is also observed that as particle size decreased, the amount of heavy metals (Cr, Cu, As) leached from the bottom ash increased.

3.3. Adsorption Characteristics

The removal rate of the different sizes of the adsorbent is shown in Fig. 1. The results show that the extent of adsorption increases rapidly in the initial stages and becomes slow in the later stages until it reaches equilibrium. Of the three particle size range, <1.19 mm demonstrated the highest and fastest adsorption of Pb since it has the largest specific surface area compared to other sizes. The surface area is generally the primary determinant of adsorption capacity [6].

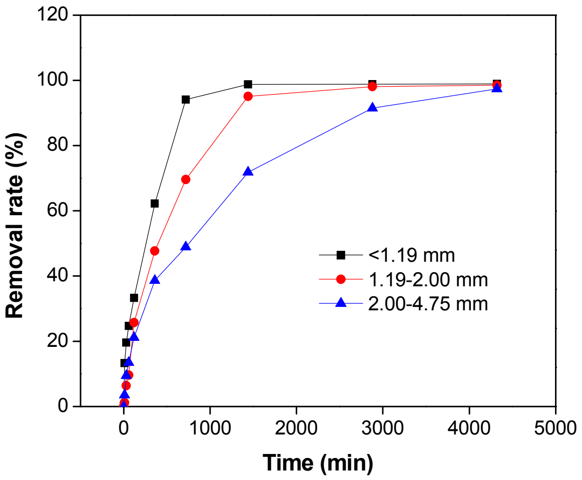

Figure 1. Adsorption capacity of adsorbent.

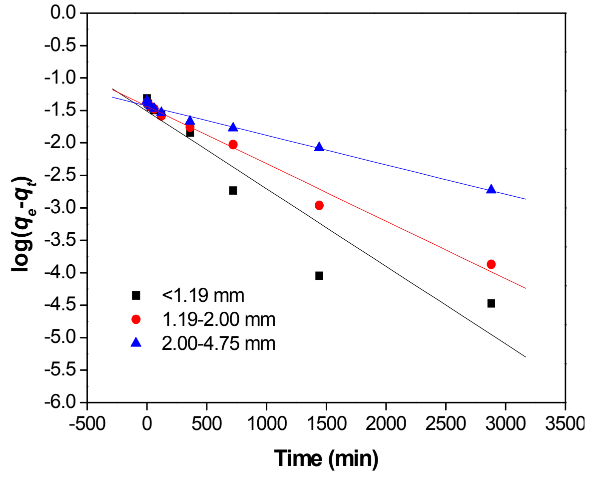

Figure 2. Pseudo-first order sorption plot.

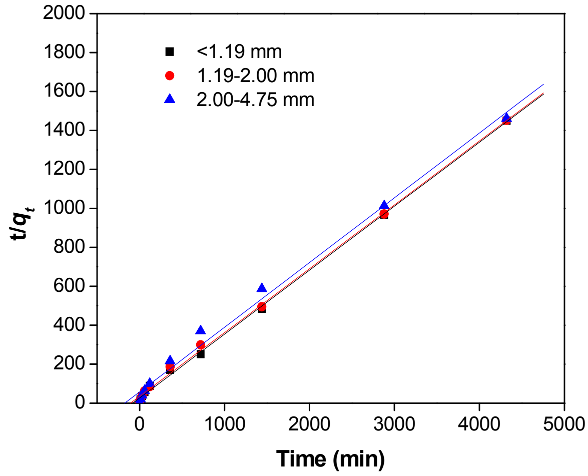

Figure 3. Pseudo-second order sorption plot.

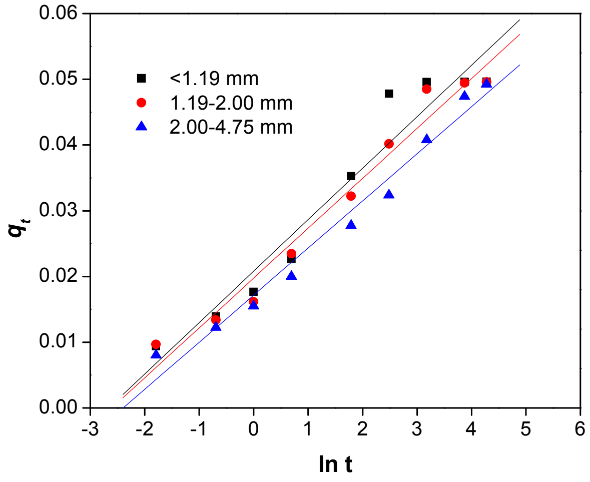

Figure 4. Elovich equation plot.

1) Kinetic models

Assuming a first order kinetic, the Lagergren equation (1) was used to determine the pseudo-first order [7].

$$\log(q_e - q_t) = \log(q_e) - \frac{K}{2.303}t \tag{1}$$

where q_t (mg g^{-1}) is the amount of adsorbate absorbed at time t (min), q_e (mg g^{-1}) is the adsorption capacity in equilibrium, and K (min^{-1}) is the rate constant for pseudo-first-order model. The pseudo-second-order model can be presented in (2)[8]:

$$\frac{t}{q_t} = \frac{1}{K_s q_e^2} + \frac{t}{q_e} \qquad (2)$$

where K_s is the rate constant of pseudo-second-order model (g $\text{mg}^{-1}\text{min}^{-1}$). Based on the 2nd order model, the initial adsorption rate (h_0) and the half adsorption time ($\tau^{1/2}$) can be estimated according to (3) and (4):

$$h_0 = K_s q_e^2 \qquad (3)$$

$$\tau^{1/2} = 1/K_s q_e \qquad (4)$$

The Elovich model is given by (5) [9]:

$$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln t \qquad (5)$$

where α and β are the parameters of the Elovich rate equation obtained by linear regression analysis of the $q_t = F(t)$ function.

Table 3. Parameters of the kinetic constants for Pb adsorption.

Particle size range	Pseudo-first		Pseudo-second				Elovich equation		
	K	R^2	K_s	h_0 x 10^4	$\tau^{1/2}$	R^2	β	α	R^2
<1.19 mm	0.015	0.777	0.250	0.615	80.7	0.999	2.129	0.112	0.945
1.19-2.00 mm	0.010	0.723	0.186	0.458	108.3	0.998	2.196	0.102	0.971
2.00-4.75 mm	0.005	0.756	0.116	0.282	174.8	0.993	2.325	0.079	0.978

Table 4. Comparison of experimental qe (mg g-1) with those predicted by the theoretical models.

Particle size range	Experimental	Pseudo-first order	Pseudo-second order
<1.19 mm	0.0497	0.504	0.0509
1.19-2.00 mm	0.0496	0.227	0.0509
2.00-4.75 mm	0.0496	0.098	0.0501

Table 5. Parameters of the equilibrium constants for Pb adsorption.

Particle size	Langmuir Isotherm			Freundlich Isotherm		
	Q_o	b	R^2	K_f	$1/n$	R^2
<1.19 mm	0.113	30.107	0.997	0.091	0.127	0.502
1.19-2.00 mm	0.114	4.419	0.998	0.077	0.212	0.844
2.00-4.75 mm	0.042	74.643	0.718	0.040	0.070	0.566

Shown in Figs. 2 to 4 are the results of the adsorption kinetics data fitted through the three theoretical models. The corresponding kinetic parameters extracted from the different equations are compiled in Table 3.

These equations were linearized and the linear coefficient of determination (R^2) was used to determine the adequateness of the different models to fit the adsorption process. A trend in the rate constants showed that K, Ks, and α increased as the particle size decreased while β increased with the particle size. This can be attributed to the available adsorbing sites on the surface of the adsorbent. The pseudo-second order equation gives the most consistent determination coefficients (R^2= 0.993~0.999) with satisfactory fittings (p<0.0001) among the three equations. Moreover, the amount adsorbed (q_e) predicted by the pseudo-second order model agrees better with the experimental data, as shown in Table 4.

2) Equilibrium isotherm models

The adsorption data were analyzed by different sorption isotherms such as Langmuir and Freundlich. The rearranged Langmuir isotherm can be presented by (6) [10]:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad (6)$$

where Q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The maximum sorption capacity (Q_0) represents monolayer coverage of sorbent with adsorbate while b represents enthalpy of sorption. The Freundlich adsorption isotherm is represented by (7)[11]:

$$log q_e = log K_f + 1/n log C_e \qquad (7)$$

where K_f and $1/n$ are Freundlich constants related to adsorption capacity and intensity of adsorption respectively.

According to the equilibrium linear plots presented in Figs. 5 and 6 and equilibrium isotherm constants shown in Table 5, Langmuir isotherm model could reasonably fit the data, with a highest correlation coefficient compared to Freundlich isotherm model. Freundlich isotherm is an indication of surface heterogeneity of the adsorbent while the Langmuir isotherm hints toward surface homogeneity of the adsorbent. The rate of the extent of adsorption was proportional to the specific surface area or the particle size. Therefore, both rate and extent of adsorption accomplished per unit weight of a solid adsorbent are expected to increase using more fine and porous materials.

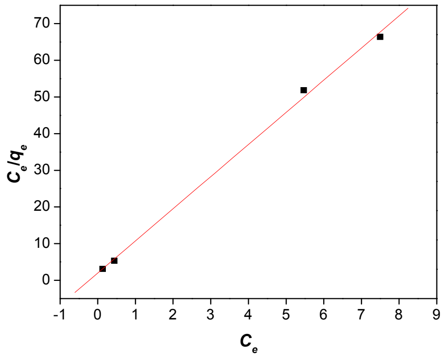

Figure 5. Langmuir isotherm plot (1.19-2.00 mm).

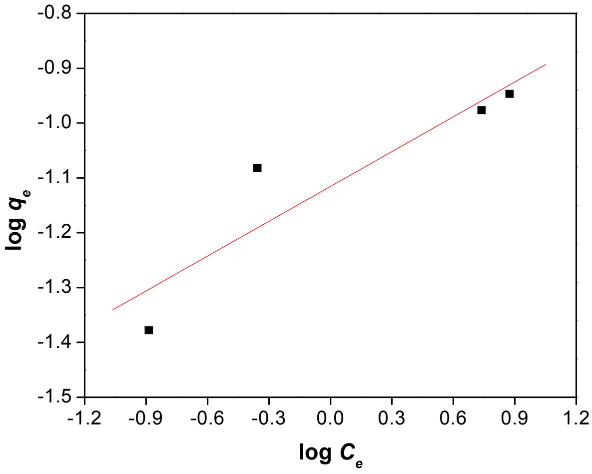

Figure 6. Freundlich isotherm plot (1.19-2.00 mm).

4. Conclusions

This study provides an opportunity to understand the adsorption process for potential reutilization of bottom ash. The results obtained in this study are as follows:

1) As particle size becomes finer, the surface area increases. Hg and Pb metals were leached from the bottom ash during KSLT and concentrations for Cr, Cu, As and Cd were found to be less than 0.3 ppm passing the Korean regulatory limit.
2) The rate of extent of leaching and adsorption is proportional to the specific surface area and particle size of the adsorbent.
3) It was observed that as particle size decreased, the amount of heavy metals (Cr, Cu, As) leached from the bottom ash and the adsorption rate for Pb increased.
4) The kinetic adsorption is best described by the pseudo-second order reaction which provides the best correlation of the data.
5) The experimental results analyzed by using the Langmuir and Freundlich isotherms, and the correlation coefficients for fitting Langmuir equation was significantly better than Freundlich isotherms.

5. Acknowledgment

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