Design of structure of hierarchically porous carbon monoliths with magnetic properties for high efficiency in adsorption of lead (II) ions

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Abstract. Pb (II) is one of the toxic heavy metal ions, which is released from the industry, especially the manufacture of batteries and electronics-devices. Its release into the water effluents causes environmental problems and affects the humans’ and animals’ health. Adsorption is one of the conventional techniques for removal of Pb (II) in water treatment processes. The adsorbents with effective adsorption properties with their easy operation are then desired. In this study, hierarchically porous carbon monoliths with magnetic properties have been designed and successfully fabricated by incorporating sodium alginate and black liquor in ferric chloride solution. The resulting monoliths have been used to study their adsorption efficiency towards Pb (II) in aqueous solution. The interconnected macroporous structures of the materials were generated by the freeze-drying process, while the increase in microporosity was observed after pyrolysis at 700 °C (SA-BL-Fe-700). SA-BL-Fe-700 showed a magnetization of 8.79 emu/g, and high porosity, with a BET specific surface area of 945.45 m²/g and pore size distribution calculated by DFT was less than 2 nm, which is suitable to adsorb Pb (II) ions. Furthermore, the materials obtained showed a monolith feature in a cylindrical shape with strong mechanical stability, which renders them with the easy operation. The adsorption properties of SA-BL-Fe-700 monolith toward Pb (II) ions demonstrated a maximum adsorption capacity of 75.19 mg/g at pH 5 with retaining the magnetic properties. The study of adsorption behaviours illustrated that equilibrium data and kinetic study fitted with Langmuir isotherm model and pseudo-second-order model, respectively.
1. Introduction
Magnetic porous carbon adsorbents have been attractive for removal of various contaminants from aqueous solution over activated carbon due to the simple separation by external magnet after complete adsorption [1]. Nonetheless, in the form of fine powder, the homogeneity of magnetic properties in each carbon particle is relatively difficult to control and could lead to secondary contamination from the non-magnetic carbon particles [2]. To address this issue, magnetically porous carbon monoliths are more desirable. The design of magnetically porous carbon monoliths used as adsorbents have not been reported before. Furthermore, their synthesis procedures were complicated and time-consuming. In this work, we therefore have designed a new strategy to fabricate magnetically porous carbon monoliths in a greener and facile manner by using the industrial wasted black liquor (BL) as a carbon precursor.

In our developed synthesis protocol, sodium alginate (NaAlg) was chosen as a carbon template because the freeze-dried NaAlg is capable of generating macroporous structures [3] which provides a rapid transportation of target molecules. In addition, the use of wasted product from Kraft process [4] by paper industry, so-called black liquor (BL) is presented. The large fraction of lignin and basic solution (NaOH/KOH) in BL could enhance mechanical stabilities and act as activation agent to increase porosity [5], respectively. Also, the -OH functional group presented in both NaAlg and BL could promote their good compatibility. Besides, the incorporation of magnetic particles can easily be performed only by adding Fe$^{3+}$ ions during the synthesis [6]. Hence, the simple one-pot synthesis of the novel magnetically hierarchical porous carbon monoliths is here demonstrated by mixing of NaAlg and BL in Fe$^{3+}$ solution via freeze-drying process and subsequently pyrolysis. To evaluate the adsorption study, lead (II) ions were selected as a representative of heavy toxic pollutant contaminated in various manufacturings such as metal plating, lead batteries, and electronic industry [7]. Because of its non-biodegradable, even in the low concentration of Pb (II) causes serious effects to environmental and living being [8]. Therefore, Pb (II) urgently needs to be removed from wastewater stream.

2. Methodology
2.1 Preparation of hierarchically porous carbon monoliths with magnetic properties
2.0 g of sodium alginate and 2.0 g of dried BL were mixed by using 25 ml of 1%w/v of FeCl$_3$·6H$_2$O solution. After the homogeneously dark-brown viscous solution had been obtained, 1.5 ml of that solution was filled in 24-well plate mould with 1.6 cm diameter. Then, the samples were frozen at -4 °C before freeze-drying process at -80 °C. The sample obtained from this step was denoted as SA-BL-Fe. After that, SA-BL-Fe was pyrolyzed either at 700 or 800 °C for 1 h under nitrogen atmosphere with 1 °C/min of heating rate. The obtained magnetic carbon monoliths were washed with hot DI water until the pH of washed solution was neutral in order to remove ashes and salt products. The final magnetic carbon monoliths were denoted as SA-BL-Fe-700 and SA-BL-Fe-800, depending on the pyrolysis temperature. The magnetic carbon monoliths were characterized using Field Emission Scanning Electron Microscope (FESEM) equipped with Energy-dispersive X-ray spectroscopy (EDS), Fourier-transform infrared spectroscopy (FT-IR), N$_2$ sorption analysis, X-ray diffraction (XRD), Vibrating Sample Magnetometry (VSM), Thermogravimetric Analysis (TGA) and universal testing machine (compression mode).

2.2 Batch adsorption studies
Adsorption experiments of SA-BL-Fe-700 towards Pb (II) ions were carried out in batch mode with 0.03 g of adsorbent. The effect of pH on adsorption performance was studied in the range of 3, 4 and 5 pH adjusted by using 0.1 M HCl and 0.1 M NaOH in 100 ml of 100 ppm Pb (II) solution for desired time. After complete adsorption experiments, magnetic porous carbon monoliths were conveniently separated from the solution by using external magnet. The concentrations of Pb (II) ion before and after adsorption experiments were determined using calibration method with Inductively coupled...
plasma - optical emission spectrometry (ICP-OES). The equilibrium adsorption capacity, $q_e$ (mg/g) of Pb (II) on SA-BL-Fe-700 was calculated using equation (1):

$$q_e = \frac{V (C_0-C_e)}{m}$$

where $C_0$ and $C_e$ were the concentrations of Pb (II) (mg/L) of initial and equilibrium time, respectively. $V$ is the volume of Pb (II) solution (L), and $m$ is weight of SA-BL-Fe-700 (g).

3. Results and Discussion:
3.1 Characterizations of SA-BL-Fe-700 monolith

TGA/DTG profile of SA-BL-Fe on Figure 1a exhibits 2 main steps of degradation; the first step was the evaporation of the moisture at the temperature below 150 °C and the following step was the degradation of the alginate-black liquor composite during 150-800 °C [3]. SA-BL-Fe contained the water content up to 30% as a result of -OH functional group on alginate and NaOH/KOH activating agent in BL, which were sensitive to capture the moisture (hygroscopic). The pyrolysis temperature caused a serious effect on mechanical stabilities of the prepared adsorbent. At 800 °C, SA-BL-Fe product cannot retain the primitive shape and was destructed into a powder form. However, SA-BL-Fe-700 exhibited a strong mechanical stability presented in the compressive stress strain curve on Figure 2b. The data illustrate that the compressive stress of SA-BL-Fe-700 was 6 times higher than that of SA-BL-Fe at 20% strain. Although SA-BL-Fe-700 has a rough curve due to the different sizes of macroporous structures, the excellent mechanical stabilities were retained. For this reason, it was suitable for applying in adsorption experiment.

![Figure 1](image1.png)

**Figure 1** a; TGA/DTG profile of SA-BL-Fe and b; Compressive stress-strain curves of SA-BL-Fe and SA-BL-Fe-700

The digital picture of SA-BL-Fe and SA-BL-Fe-700 was shown in Figure 2a. The size of carbonized material was reduced from 1.5 cm of diameter and 0.8 cm of height to 1.0 and 0.5 cm, respectively. It is noticed that the shrinkage of materials occurred during pyrolysis process by only ~30%.

FESEM images in Figure 2 demonstrate the surface morphology of SA-BL-Fe-700 with the abundant macropores. The larger macropores (~150 μm) (Figure 2b) and the smaller one (<10 μm) (Figure 2c) were generated during the synthesis probably due to the freeze-drying process [3]. The EDS-mapping results were revealed on Figure 2d and show that SA-BL-Fe-700 possessed the elemental compositions of C (77.8 wt%), O (12.6 wt%), Fe (6.2 wt%), Ca (1.2 wt%), S (0.8 wt%), Na (0.7 wt%), Si (0.4 wt%) and K (0.3 wt%). The present of inorganic elements such as Ca, S, Si and K could be directly from BL precursor. Although there are some of iron clusters on the materials, the good distribution of iron particles is still obviously seen (Figure 2d).

$N_2$ sorption isotherm of SA-BL-Fe-700 from Figure 3a was used to describe pore texture of the material, which exhibits type I isotherm as a result of an existence of abundant microporous structure (size <2 nm). Pore size distribution in Figure 3b calculated by using Density Functional Theory (DFT) illustrates the sharp distributed micropore size of 1.18 nm, further supporting the sorption isotherm data. Both NaOH/KOH from BL and Fe$^{3+}$ from the solution could behave as activating
agents and help promote the generation of high porosity of SA-BL-Fe-700 with a high surface area of 945.45 m²/g. [9]

**Figure 2** a; photograph of SA-BL-Fe and SA-BL-Fe-700 b,c; FESEM images of SA-BL-Fe-700 with difference magnification and d; EDS-mapping of SA-BI-Fe-700 and its elemental compositions.

Besides, the reduction of trivalent iron (Fe³⁺) to zero-valent iron (Fe⁰) occurred during the pyrolysis process as confirmed by XRD pattern in Figure 3c. There are 3 main characteristic peaks of ferrite or Fe⁰ (ICDD file no. 00-006-0696) at 20 positions of 44.67, 65.023 and 82.33 ° belonging to (110), (200) and (211) planes, respectively. Moreover, XRD pattern of SA-BL-Fe-700 revealed 2 diffraction broad peaks of turbostratic carbon at 20 values 26.2° and 43° in (002) and (100) plane, respectively. The present of zero-valent Fe in SA-BL-Fe-700 make the material possess a great saturation magnetization of 8.7936 emu/g (Figure 3d). The inset in Figure 3d reveals the high stable magnetic properties of adsorbent and it can float under the surface of Pb (II) solution even after adsorption experiment.

### 3.2 Batch adsorption studies

SA-BL-Fe-700 exhibits the high stability against acid leaching (Figure 3e) in the range of pH > 2. Since the precipitation of lead hydroxides [8] occur under basic conditions (pH ≥ 6), improper to be used to study the adsorption. Hence, the effect of initial pH on adsorption capacity was operated in the pH rage of 3-5. Figure 3f shows the equilibrium adsorption capacity of Pb (II) ion reached the maximum at pH 5. At pH 5, the adsorption driving force involves the highest degree of electrostatic attraction, the least positive charge on the surface of sample. This behaviour is consistent with the zeta potential results (see Figure 3g).

Figure 3h presents the effects of contact time on Pb (II) adsorption by SA-BL-Fe-700 investigated with the initial concentration of 200 ppm Pb (II) at pH 5. The initially rapid adsorption was observed and reached the equilibrium within 200 min. To evaluate the adsorption kinetics, the collected data were fitted with non-linear equation of pseudo-first-order and pseudo-second-order model, as presented in Table 1. The kinetic model of SA-BL-Fe-700 was well fitted with pseudo-second-order models for Pb (II) adsorption; the determination coefficient (R²) is 0.9988 and the experimental and calculated qe values are identical (137 and 140.84 mg/g, respectively). Due to the hierarchically porous structure, the sample provided a rapid transportation. The kinetic rate is relatively fast (k = 4.33×10⁴ g mg⁻¹ min⁻¹) even in the monolithic form in comparison with powdery samples in other works (Table 2).

To study the adsorption mechanism in detail, the intra-particle diffusion model was used as parameters. Figure 3i illustrates the plot of adsorption capacity at different time intervals (qe, mg/g) as a function of t₁/₂ (min¹/²). The separation of 2 linear lines is obviously seen, suggesting that more than one physical process controls the adsorption rate. The first step occurs during 0-60 min which had
A high value of $k_{id} = 9.511 \text{ mg g}^{-1} \text{ min}^{-1}$ indicating to the rapid film adsorption. The following step occurs during 90-600 min with the slow $k_{id}$ of 0.920 $\text{ mg g}^{-1} \text{ min}^{-1}$ involving to the intra-particle diffusion step which is rate limiting step. The interaction between adsorbent and Pb (II) could further be explained by FT-IR (Figure 3j). The more positive site on the oxygen-containing functional groups provides more ability for the sharing or exchange electron with the Pb (II) ions. This behavior was confirmed by the presence of functional groups such as $-\text{OH}, \text{CH}_2, \text{C}=\text{O}$ and $\text{C}-\text{O}$ at 3411, 2918, 1579, 1400 and 1058 cm$^{-1}$ respectively, is shifted after Pb (II) adsorption [7].

To examine the adsorption isotherm, the collected data were fitted with non-linear equation of Langmuir and Freundlich adsorption models (Table 1). The perfect fit with Langmuir adsorption model ($R^2 = 0.9960$) suggests the monolayer adsorption. The maximum adsorption capacity ($q_m$) is 75.19 mg/g which is comparable to those of other magnetically powder adsorbents (Table 2).

![Figure 3](image.png)

**Figure 3** a; N$_2$ sorption isotherm, b; pore size distribution, c; XRD pattern, d; magnetic hysteresis loops, e; the stabilities of SA-BL-Fe-700 against acid conditions, f; effects of initial pH on adsorption performance of SA-BL-Fe-700, g; zeta potential of SA-BL-Fe-700; h; effects of contact time on Pb (II) adsorption by SA-BL-Fe-700, i; intraparticle diffusion plot for Pb (II) removal and j; FT-IR spectrum of SA-BL-Fe-700 before and after adsorption

| Model and Parameter               | $q_{(cal)}$ (mg/g) | $q_{(exp)}$ (mg/g) | $k$          | $R^2$      |
|----------------------------------|-------------------|-------------------|--------------|------------|
| Pseudo first order               | 70.31             | 137               | 4.34$\times10^{-4}$ (min$^{-1}$) | 0.8227     |
| Pseudo second order              | 140.84            | 137               | 4.33$\times10^{-4}$ (g mg$^{-1}$ min$^{-1}$) | 0.9988     |
| Intra-particle diffusion at 0-60 min | 9.511            | 34.645            | X            | R$^2$      |
| Langmuir adsorption              | $q_m$ (mg/g) = 75.19 | $k_L$ (L/mg) = 0.21 | $R^2 = 0.9960$ |            |
| Freundlich adsorption            | $k_F = 51.99$     | $1/n = 0.0626$    | $R^2 = 0.5679$ |            |
he prepared carbon monoliths are attractive for applying in adsorption of other pollutants and in other applications such as catalyst supports. Hierarchically porous carbon monoliths with magnetic properties were successfully fabricated via a facile freeze-drying and subsequent pyrolysis process, generating the macroporous and microporous structures, respectively. The high BET specific surface area (945.45 m²/g) and suitable micropore size (1.18 nm) promote good adsorption of Pb (II) with the maximum adsorption capacity of 75.19 mg/g at pH 5. Herein, the simple preparation method of SA-BL-Fe-700 is considered to be the promising method for large-scale synthesis of magnetic porous carbon monoliths as good adsorbents. For the next improve, the prepared carbon monoliths are attractive for applying in adsorption of other pollutants and in other applications such as catalyst supports and energy storage devices.

**Table 2** Comparison of preparation method to Pb (II) adsorption performance of magnetic carbon materials

| Materials/ adsorbent | Methods                                      | S\textsubscript{BET} [m²/g] | q\textsubscript{m} [mg/g] | pH | k [g mg\textsuperscript{-1} min\textsuperscript{-1}] | T [K] | Magnetizations [emu/g] | Ref. |
|----------------------|----------------------------------------------|-----------------------------|---------------------------|----|----------------------|-------|------------------------|------|
| powder               | Modified activated carbon                    | -                           | 93.45                     | 5.5| 6.0 × 10\textsuperscript{-2} | 298   | 12                     | [11] |
| powder               | Silica template                              | 431                         | 66.2                      | 6-7| -                    | 298   | 50.67                  | [12] |
| powder               | Pyrolysis and KMnO\textsubscript{4} activation | 137                         | 148                       | >  | 3.67 × 10\textsuperscript{2} | 298   | 11.5                   | [13] |
| SA-BL-Fe-700 (monolith) | Freeze-drying and pyrolysis                | 945.45                      | 75.19                     | 5  | 4.33 × 10\textsuperscript{4} | 303   | 8.79                   | This work |

**Conclusion:**
Hierarchically porous carbon monoliths with magnetic properties were successfully fabricated via a facile freeze-drying and subsequent pyrolysis process, generating the macroporous and microporous structures, respectively. The high BET specific surface area (945.45 m²/g) and suitable micropore size (1.18 nm) promote good adsorption of Pb (II) with the maximum adsorption capacity of 75.19 mg/g at pH 5. Herein, the simple preparation method of SA-BL-Fe-700 is considered to be the promising method for large-scale synthesis of magnetic porous carbon monoliths as good adsorbents. For the next improve, the prepared carbon monoliths are attractive for applying in adsorption of other pollutants and in other applications such as catalyst supports and energy storage devices.

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