Removal of lead and bisphenol A using magnesium silicate impregnated palm-shell waste powdered activated carbon: Comparative studies on single and binary pollutant adsorption

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ABSTRACT

In this work, palm shell waste powder activated carbon coated by magnesium silicate (PPAC-MS) were synthesized by the impregnation of magnesium silicate (MgSiO3) using economical material (silicon dioxide powder) via mild hydrothermal approach for the first time. As an effective adsorbent, PPAC-MS simultaneously removes BPA and Pb(II) in single and binary mode. Surprisingly, PPAC-MS exhibited a homogeneous thin plate mesh-like structure, as well as meso- and macropores with a high surface area of 772.1 m² g⁻¹. Due to its specific morphological characteristics, PPAC-MS had adsorption capacities of Pb(II) as high as 419.9 mg g⁻¹ and 408.8 mg g⁻¹ in single mode and binary mode based on Freudlich isotherm model while those for BPA by PPAC-MS were 168.4 mg g⁻¹ and 254.7 mg g⁻¹ for single mode and binary modes corresponding to Langmuir isotherm model. Experiment results also indicated that the synergistic removal of BPA occurred because the precipitation process of Pb(II) leads to the co-precipitation of BPA with Pb(OH)2 compound. PPAC-MS showed a good reusability for 5 regeneration cycles using Mg(II) solution followed by thermal treatment. Overall, PPAC-MS has a high potential in the treatment process for wastewater containing both toxic heavy metals and emerging pollutants due to its high sorption capacities and reusability.

1. Introduction

Effluents discharged from industry wastewater contain high concentrations of heavy metals, causing a serious environmental and health problems. Metals such as arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg) and selenium (Se) are dangerous to human and animals due to their toxicities (Simato and Ndlovu, 2014). Especially, Pb(II) can be frequently found in industrial wastewater from active or abandoned mine, battery industry and metal pelting industry. Pb(II) excess can give an effect on erythropoiesis that decreases oxygen level in blood circulation, neutral deafness, kidney and liver damage and causes drop in an intelligence quotient (IQ) for children and cause a reduction in numbers of leaves, leaf area and plant height (Chibuike and Obiora, 2014; Mudga et al., 2010).

Apart from heavy metals in the wastewater, micropollutants could coexist in industry wastewater (Lee et al., 2015; Mohapatra et al., 2011). Especially, bisphenol A (BPA) is one type of endocrine disrupting chemicals (EDCs) which can cause hazardous health effects on humans. As BPA has been widely used in manufacturing of epoxy and polycarbonate, it is highly resistant for chemical degradation. Moreover, even at a low concentration, BPA can disrupt the endocrine system in human being (Liu et al., 2016).

Currently, since many surface waters are contaminated by both organic and inorganic toxic compounds, it is necessary to develop high efficiency media that can remove both toxic compounds simultaneously. As one of the most promising methods, adsorption of Pb(II) or BPA by activated carbon has been extensively studied (Bautista-Toledo et al., 2005; Gaya et al., 2015; Kadirvelu et al., 2000; Shekinah et al., 2002; Xu et al., 2012). However, there is few studies that have been conducted on the simultaneous removal of BPA and Pb(II). Foo and Hameed (2012) investigated preparation of activated carbon from oil palm shell waste demonstrated great potential on Methylene blue removal. Moreover, Chong et al. (2013) also reported oil palm shell waste activated carbon revealed as the potential filter bed media for wetland application.

In this study, palm-shell waste powdered activated carbon (PPAC) or PPAC modified by magnesium silicate (MgSiO3) (PPAC-MS) was used or prepared to remove both Pb(II) and BPA from the synthetic solution.
for the first time. To prepare PPAC-MS, MgSiO$_2$ was impregnated on PPAC under hydrothermal treatment in an economical route using a cheap precursor (silicon dioxide powder). Material characteristics such as Fourier Transform Infrared (FTIR), nitrogen adsorption-desorption isotherms, field emission scanning electron microscopy (FESEM), energy dispersed X-Ray (EDX) and X-Ray diffractometer (XRD) were performed on PPAC, PPAC-MS, used PPAC after binary mode adsorption (designated as UPPAC) and used PPAC-MS after binary mode adsorption (designated as UPPAC-MS). The adsorption isotherms and kinetics of Pb(II) and BPA by PPAC and PPAC-MS were determined in single and binary modes. Furthermore, the mechanism of BPA and Pb (II) removal was discussed through interconnecting between characterization and batch results.

2. Materials and methods

2.1. Materials

PPAC activated by potassium hydroxide (KOH) was obtained from Bravo Green Sdn. Bhd, Malaysia pass through mesh size 200 (< 75 µm). Then, it was washed with distilled water more than 3 times until washed water electro-conductivity was less than 300 µs cm$^{-1}$ and oven dried at 70 °C for 24 h. Sodium chloride (NaCl), BPA, silicon (SiO$_2$), magnesium oxide (MgO), methanol, lead nitrate (Pb(NO$_3$)$_2$), sodium hydroxide (NaOH) and nitric acid (HNO$_3$) obtained from R & M chemical were of analytical grade. Lead test kit [4-2′-(pyridylazo) resorcinol (PAR)] was obtained from Merck Company.

2.2. Preparation of PPAC-MS

Three point three g of MgO and 4.80 g of SiO$_2$ were added in 50 mL of deionized water. Then, the suspension was stirred continuously to get a white colored magnesium silicate gel. Ten g of PPAC was added for this suspension. Then the PPAC and suspension were continuously stirred at 150 rpm for 1 h at 24 ± 1 °C using a magnetic stirrer hotplate (Dragon Lab MS-H280-Pro). The mixture was transferred into a stainless-steel Teflon-lined autoclave and treated for 10 h at 150 °C. The resulted product was filtered through a 0.45 µm-pore Whatman filter paper and washed with distilled water more than 3 times, and dried in an oven at 70 °C for 24 h.

2.3. Material characterization

The surface chemical characteristics of PPAC and PPAC-MS were determined by Fourier Transform Infrared (FTIR) (Perkin Elmer, FTIR-spectrum 400) in the range of 4000 – 450 cm$^{-1}$. Nitrogen adsorption-desorption isotherm was obtained to measure surface areas, pore volume and pore size distribution using Micromeritics ASAP2020 (Tristar II 3020). The degassing was operated at 300 °C for 4 h. The surface area was determined by Langmuir, Barrett Joyner-Halenda (BJH) and BET. Pore size distribution was also calculated using BET and BJH equation and pore volume was calculated by BJH. The surface morphologies of PPAC and PPAC-MS were determined by FESEM-EDX (PEG Quanta 450, EDX-OXFORD and Hitachi SU8010). The morphology of samples were observed directly by FESEM without any coating. The XRD patterns of materials were also obtained using X-Ray diffractometer (EMPyREAN, PANalytical) with the voltage of 40 kV and 40 mA anode current of Cu Kα radiation. The XRD data were recorded in the range of 10 – 80° at 0.02 step size. The XRD raw data was evaluated using the Highscore software (PANalytical).

2.4. Adsorption isotherms

The isotherm experiments were carried out with 0.005 g of adsorbents with 50 mL of single pollutant (either BPA or Pb(II)) or mixed pollutants (BPA and Pb(II)) containing solutions under 150 rpm for 24 h (Shaker, Lab Companion, SK-300). The Pb(II) solution (25 – 400 mg L$^{-1}$) was prepared using Pb(NO$_3$)$_2$ in deionized water. The prepared concentration of BPA solution was 10 – 100 mg L$^{-1}$ in deionized water. The combined solution of BPA and Pb(II) was designated as ‘x+y’ where ‘x’ is the concentration of BPA and ‘y’ is the concentration of Pb(II). The concentrations (mg L$^{-1}$) of binary pollutants in solution were expressed e.g. “100+400”, “80+300”, “60+200”, “40+100”, “20+50” and “10+25” in deionized water (Liu et al., 2016). All the solutions were adjusted to pH 4.5 using 0.1 M of sodium hydroxide (NaOH) and nitric acid (HNO$_3$) at 24 ± 1 °C (Goel et al., 2005; He et al., 2015). When the reaction was completed, the suspension was collected and filtered through a 0.45 µm-pore Whatman filter paper. After isotherm experiments, Pb(II) concentrations were determined using the 4-(2′-pyridylazo) resorcinol (PAR) colorimetric method using standard Merck kit and BPA concentrations were measured using a UV spectrophotometer (Merk, Spectrophotometric methods (Greenberg et al., 1992)).

2.5. Adsorption kinetics

AdSORption kinetics were performed using 0.005 g of PPAC and PPAC-MS with 50 mL of pollutant solutions under 150 rpm at 24 ± 1 °C. Two hundred mg L$^{-1}$ of Pb(II) and 50 mg L$^{-1}$ of BPA solutions were prepared for kinetics in both single and binary pollutant modes to investigate the influences of BPA in Pb(II) removal. Samples were collected at a different time interval in the range of 10 min to 3 h. And then, the collected samples were analyzed for Pb(II) and BPA concentrations. To analyze kinetic adsorption process, the pseudo-first and pseudo-second order kinetics models (referred SI) were applied.

2.6. Effect of Pb(II) precipitation on BPA removal

Different initial concentration of Pb(II) (25 – 400 mg L$^{-1}$) and BPA (10 – 100 mg L$^{-1}$) solution were prepared and its pH was adjusted to 4.5 to avoid metal hydrolysis. Meanwhile, in order to investigate the co-precipitation of BPA by Pb(OH)$_3$, Pb(II) was precipitated by adjusting solution pH to 7 without adding sorption media under 150 rpm for 24 h at room temperature. The supernatant was drawn out for BPA concentration measurement at pH 7. Then, the remaining suspension was treated using 0.1 M of HNO$_3$ to adjust pH to 2.5 under 150 rpm for 24 h at room temperature. When the reaction was completed, the suspension was collected and filtered through a 0.45 µm-pore Whatman filter paper for analyzed the residual concentration of BPA. The residual BPA concentrations were measured using a UV spectrophotometer (Merk, Spectrophotometric methods (Greenberg et al., 1992)).

The surface characteristics of precipitant of Pb(II) with BPA (designated as PLB) was determined by FTIR analysis. The Visual MINTEQ. 3.1 were also used to calculate the saturation index (SI) and ion activity product (IAP). If the SI is > 0, it means that the minerals are oversaturated, if SI is < 0, it represents that the phases of minerals are undersaturated. On the other hand, if SI is equal to 0, the solid reaches an equilibrium.

2.7. Ionic strength effect on BPA and Pb(II) removal by PPAC and PPAC-MS

Bautista-Toledo et al. (2005) and Bou dredahem et al. (2011) reported the presence of salt affects on the sorption of BPA and Pb(II) in aqueous phase and thereby the influences of ionic strength on the removal of BPA and Pb(II) by PPAC and PPAC-MS were investigated. Five mg of adsorbent was added into 50 mL solution containing 400 mg L$^{-1}$ Pb(II)
and 100 mg L\(^{-1}\) BPA with various concentrations (0.01 – 0.05 mM) of ionic strength by sodium chloride (NaCl).

### 2.8. Regeneration of Pb(II) and BPA retained PPAC-MS

To investigate the reusability of PPAC-MS, 5 cycles of adsorption and desorption experiments were conducted. To the best of our knowledge, the present study was the first reported study that the adsorbent was desorbed by Mg(II) solution followed by thermal treatment. Five mg with 50 mL solution containing 400 mg L\(^{-1}\) Pb(II) and 100 mg L\(^{-1}\) BPA was shaken under 150 rpm at room temperature (24 ± 1 °C) for 24 h. After adsorption, pollutants retained media were treated with 50 mg L\(^{-1}\) of Mg(II) solution. This suspension was shaken under 150 rpm at 24 ± 1 °C for 1 h. Then, the adsorbent was heated at 350 °C for 3 h. The adsorbent was washed more than 3 times with distilled water to remove loose MgSiO\(_3\) on the surface of PPAC and dried in oven at 70 °C for 24 h to dry out the moisture from the adsorbents for another adsorption (Yousefi, 2014).

### 3. Results and discussion

#### 3.1. Adsorption isotherms of Pb(II) and BPA

Figs. 1 and 2 present adsorption isotherms of Pb(II) and BPA by PPAC and PPAC-MS in single and binary modes, as well as data fits by use of Langmuir and Freundlich models. According to the determination coefficient (R\(^2\)) in Table S1 (refer SI), the adsorption of Pb(II) by PPAC apparently fitted well to the Langmuir isotherm while that of PPAC-MS better fitted with the Freundlich isotherm. Thus, these fitting results inferred that Pb(II) can absorb as homogeneously monolayer on PPAC while it retains as heterogeneous multilayer for PPAC-MS both in single and binary mode (Cataldo et al., 2016). On the other hand, the adsorption of BPA by PPAC and PPAC-MS fitted well with Langmuir model both in single and binary modes (Table S1). These results concluded that the adsorption of BPA occurs on the surface of PPAC and PPAC-MS as homogeneous monolayer adsorption. The Q\(_{\text{max}}\) (based on the Langmuir model) of Pb(II) removals by PPAC were 391.3 and 194.5 mg g\(^{-1}\) in single and binary modes, respectively, while those by PPAC-MS were 419.9 and 408.8 mg g\(^{-1}\) based on the Freundlich model. And, the maximum adsorptions of BPA in single and binary modes by the Langmuir model were 359.6 mg g\(^{-1}\) and 360.7 mg g\(^{-1}\) for PPAC while those by PPAC-MS were 168.4 mg g\(^{-1}\) and 254.7 mg g\(^{-1}\), correspondingly.

PPAC had the similar adsorption capacities of BPA in both single and binary modes, but had lower sorption capacity of Pb(II) in binary mode than single mode. Remarkably, however, the isotherm results indicated that Pb(II) removals by PPAC-MS both in single and binary modes were much higher than those by PPAC. Especially, it was found that the adsorption capacities of Pb(II) by PPAC-MS were not reduced in binary mode, but even increased, while those by PPAC greatly reduced. Accordingly, it infers that when Pb(II) and BPA coexist in the solution, they compete for available adsorption sites on the surface of PPAC. Pb(II) might be removed at the same adsorption sites with BPA at PPAC, but the PPAC surface had higher preference on BPA. Therefore, the presence of BPA reduces the number of available adsorption sites in binary mode, decreasing the adsorption capacity of Pb(II) on PPAC (Bonvin et al., 2016). Meanwhile, PPAC-MS might have different sorption sites for Pb(II) and BPA since Pb(II) and BPA removals were not reduced and even increased in binary mode, respectively.

The sorption capacities of pollutants by PPAC and PPAC-MS were
evaluated based on the surface area and pore volume. PPAC-MS has a lower surface area (772.1 m² g⁻¹) and microspore volume (0.263 cm³ g⁻¹) compared to PPAC (1099.8 m² g⁻¹ and 0.38 cm³ g⁻¹). This could be primary reason that PPAC had better sorption of BPA for both single and binary modes than PPAC-MS. Moreover, when the mineral material like magnesium silicate exist in PPAC, activated carbon become more hydrophilic to reduce the adsorption capacity of BPA (Bautista-Toledo et al., 2005). On the other hand, PPAC-MS sorption capacity increased 50% for the BPA removal in binary mode, while PPAC remains similar adsorption capacity. This is due to the fact that the surface of PPAC-MS can release hydroxide (OH⁻), resulting in the precipitation of Pb(II) ions. While the precipitation process of Pb(II) occurs, BPA can co-precipitate with the Pb(OH)₂ compounds. Therefore, in the presence of Pb(II) ions, the sorption capacity of BPA by PPAC-MS greatly increased. The effect of Pb(II) precipitation on BPA removal has been separately tested and its results were described at Section 3.3.

### 3.2. Adsorption kinetics for Pb(II) and BPA in single and binary modes

Fig. 3 presents the results of kinetics of Pb(II) and BPA by PPAC and PPAC-MS in single and binary modes. The data of adsorption kinetics were modelled using the Pseudo-first and Pseudo-second order kinetic models, in which parameters were shown in Table 1. The determination coefficients (R²) of Pseudo-second order kinetic model were much higher than those of Pseudo-first order. As a result, overall of Pb(II) and BPA adsorption process by PPAC and PPAC-MS can be concluded as chemisorption (Yakout and Borai, 2014). As the similar results with isotherms, PPAC-MS had the calculated qₑₒₑ of Pb(II) (479.7 mg g⁻¹), which was higher than PPAC (373.4 mg g⁻¹) in single mode. The equilibrium adsorption for Pb(II) was obtained after 90 min for PPAC-MS and PPAC in single mode. On the other hand, qₑₒₑ of Pb(II) by PPAC in the binary mode was 101.74 mg g⁻¹ which was only 73% of qₑₒₑ obtained at single mode whiles qₑₒₑ (485.9 mg g⁻¹) for PPAC-MS in binary mode was higher than that in single mode. The equilibrium adsorptions of Pb(II) by both PPAC and PPAC-MS were obtained at 60 min in the binary mode. Thus, Pb(II) equilibrium adsorption by PPAC and PPAC-MS occurred faster in binary mode compare to single mode. This behavior can be explained by the competition effect between BPA and Pb(II) to compete for available adsorption site (Nouri et al., 2007).

Meanwhile, qₑₒₑ for BPA removal by PPAC-MS was 101.5 mg g⁻¹ which was lower than qₑₒₑ for PPAC (277.5 mg g⁻¹) in single mode. The qₑₒₑ of BPA removal by PPAC remains as 277.5 mg g⁻¹ but PPAC was greatly increased to 121.9 mg g⁻¹ in binary mode. The equilibrium adsorption was obtained after 90 min for single and binary mode for PPAC-MS and PPAC.

### 3.3. Effect of Pb(II) precipitation on BPA removal

To investigate the BPA removal on Pb(II) precipitation, we further carried out an experiment to evaluate the relationship between Pb(II) precipitation and BPA removal in binary system. Table S3 shows the remained concentrations of BPA at different pH in the presence of Pb (II). The experiment results indicated that BPA concentrations greatly reduced at pH 7 and remained almost same as the initial concentration.
at pH 2.5. The SI calculated by the Visual MINTEQ 3.1 for all Pb(II) solution at pH 7 is more than zero which indicated the Pb(OH)$_2$ mineral phase is supersaturated. Moreover, the SI for all Pb(II) solution at pH 2.5 is less than zero, indicating that the Pb(OH)$_2$ is undersaturated (refer Table S4).

3.4. Material characteristics

To understand the mechanisms of the removal of BPA and Pb(II) by PPAC and PPAC-MS, nitrogen adsorption-desorption isotherm, BET, XRD, FESEM-EDX and FTIR analysis were conducted.

First, the surface chemical characteristics of PPAC and PPAC-MS were evaluated by use of FTIR (Fig. S1 in SI). The peaks at 3737, 3729 and 3854 cm$^{-1}$ indicated O-H stretching on PPAC and PPAC-MS. Asymmetric and symmetric C-H stretching vibration peaks were shown at 2924/2853 cm$^{-1}$ for PPAC. The peak at 1556 cm$^{-1}$ of PPAC indicated aromatic ring C=C while C-O-H group was shown at 1448 cm$^{-1}$. After magnesium silicate was impregnated on PPAC, C=C bond reduced and shifted to 1555 cm$^{-1}$. Besides that, the peak of C-O-H group remained, but shifted to 1435 cm$^{-1}$. Compared to PPAC, the peak at 1004 cm$^{-1}$ corresponds to the asymmetric Si-O-Si or Si-O-Me (Me: metal) bond. After the adsorption in binary mode, peaks at 3369 and 3422 cm$^{-1}$ with UPPAC-MS and UPPAC, respectively, represent the OH group stretching vibration. Besides that, the peak at 1552 and 1551 cm$^{-1}$ for UPPAC and UPPAC-MS, correspondingly, are characteristics of aromatic C=C bond. The functionalized group asymmetric Si-O-Si or Si-O-Me on the surface of PPAC-MS is exposed to solution and form Si-O due to the dissolution of Mg-OH. Therefore, the negatively charge Si-O functional group on PPAC-MS will be occupied by Pb metal ions in aqueous solution due to Si-O functional group consists of strong attraction toward positively charge adsorbate. Moreover, the dissolved Mg-OH- will be react with metals ion and form

<table>
<thead>
<tr>
<th>Mode</th>
<th>Pollutants</th>
<th>Media</th>
<th>$K_1$ (min$^{-1}$)</th>
<th>$R^2$</th>
<th>$K_2$ (g mg$^{-1}$ min$^{-1}$)</th>
<th>$q_{eq}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single</td>
<td>BPA</td>
<td>PPAC</td>
<td>0.013</td>
<td>0.89</td>
<td>0.0003</td>
<td>268.8</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PPAC-MS</td>
<td>0.011</td>
<td>0.81</td>
<td>0.0004</td>
<td>101.0</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>Binary</td>
<td>BPA</td>
<td>0.016</td>
<td>0.85</td>
<td>0.0005</td>
<td>272.2</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PPAC</td>
<td>0.015</td>
<td>0.85</td>
<td>0.0009</td>
<td>118.8</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PPAC-MS</td>
<td>0.015</td>
<td>0.95</td>
<td>0.0002</td>
<td>373.4</td>
<td>0.98</td>
</tr>
<tr>
<td>Single</td>
<td>Pb(II)</td>
<td>PPAC</td>
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<td>0.91</td>
<td>0.0003</td>
<td>479.7</td>
<td>0.99</td>
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<tr>
<td></td>
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<td>PPAC-MS</td>
<td>0.015</td>
<td>0.95</td>
<td>0.0001</td>
<td>485.9</td>
<td>0.98</td>
</tr>
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</table>

Fig. 3. Adsorption kinetics of Pb(II) and BPA by PPAC and PPAC-MS (dot lines fitted to Pseudo-second order kinetic model): (A) BPA removal in the single mode and (B) binary mode, (C) Pb(II) removal in the single mode and (D) binary mode.
precipitant (Nagarajah et al., 2017). After BPA adsorption, the peak at 1445/1400 cm$^{-1}$ for UPPAC/UPPAC-MS greatly increased. These peaks correspond to the C-O-H bonds and the aromatic C=C bond and C-O-H were assigned as BPA compound. The new peak at 1740 cm$^{-1}$ was recorded as C=O stretching from the carboxyl group on UPPAC which were attributed to the BPA compound (Li et al., 2004). The peaks at 2927, 2855 and 2853 cm$^{-1}$ on UPPAC and UPPAC-MS indicated the C-H bond stretching due to the alkyl chain of BPA of the grafted side chains (Guang Choo et al., 2011). The peak at 763 cm$^{-1}$ can be assigned as C-C bond stretching while the peak at 2960 cm$^{-1}$ was recorded as C=O stretching from the carboxyl group on UPPAC and UPPAC-MS had a strong peak at 1594 and 1489 cm$^{-1}$ indicated asymmetric and symmetric C-H stretching. Strong peaks at 1400 and 1450 cm$^{-1}$ were attributed to the BPA compound (Li et al., 2004). The peaks at 844, 829, 1175 and 1145 cm$^{-1}$ correspond the stretching for C-O and C-C bond in both rings (Ullah et al., 2004). The peaks at 2927, 2855 and 2853 cm$^{-1}$ on UPPAC and UPPAC-MS indicated the C-H bond stretching due to the alkyl chain of BPA of the grafted side chains (Guang Choo et al., 2011). The peak at 763 cm$^{-1}$ can be assigned as C-C bond stretching while the peak at 2960 cm$^{-1}$ on PLB indicated asymmetric and symmetric C-H stretching. Strong peaks at 1594 and 1489 cm$^{-1}$ were assigned for C=C aromatic bond and C-O-H group, respectively. The peaks at 844, 829, 1175 and 1145 cm$^{-1}$ correspond the stretching for C-O and C-C bond in both rings (Ullah et al., 2016). Aromatic C=C (1594 cm$^{-1}$), C-O-H (1489 cm$^{-1}$), C-C (1175 cm$^{-1}$) and C-O bonds (844/829 cm$^{-1}$) in BPA molecule were strongly detected on PLB surface. Thus, an increase of pH in Pb(II) solution results in the precipitation as Pb(OH)$_2$ that can sink BPA by physical co-precipitation (Sridharan and Lee, 1972).

Nitrogen adsorption-desorption isotherms indicated that PPAC and PPAC-MS were classified as type 1 and type 4 isotherms, respectively, according to International Union of Pure and Applied Chemistry (IUPAC) classification (Fig. 4A). Type I isotherm has the characteristics for a highly micro-porous material. Especially, the marked knee at 0.02 – 0.2 of P/P$_0$ and a low slope at 0.8 – 1.0 of P/P$_0$ for PPAC represented significant micropores characteristics. Contrast to PPAC, PPAC-MS had a high slope in 0.8 – 1.0 of P/P$_0$, representing the existence of meso- and macropore structures. PPAC-MS exhibited a H4 hysteresis loop, in which the adsorption and desorption curves are separate and form parallel in 0.5 – 1.0 of P/P$_0$. Fig. 4 B illustrates the pore size distributions of PPAC and PPAC-MS by BJH method. PPAC and PPAC-MS had a similar sharp peak at 32 Å with the FASS correction, indicating that the pore width at 32 Å increase after magnesium silicate impregnated on PPAC. Moreover, PPAC-MS had another pore ranging at 140 – 370 Å. BJH surface area and BJH pore volume of PPAC-MS were higher than PPAC due to the formation of macro- and meso-pores formation on PPAC-MS shown in Fig. 4B. This is because the void spaces were formed by interwoven of MgSiO$_3$ on the surface of PPAC-MS (Gui et al., 2014). Table S5 lists the pore properties of PPAC and PPAC-MS including BET and micropore surface area, as well as pore volume. Compared to PPAC-MS, PPAC had higher total surface area, BET and micropore surface area.

In order to explain the surface chemical composition of PPAC and PPAC-MS, XRD analysis was conducted (Fig. 4C). PPAC had one strong peak at 29.5° assigned as graphite (JCPDS File no. 01-0640) and broad asymmetric peaks from 25 to 50°, corresponding to typical amorphous carbon activated by KOH (Gaya et al., 2015; Khalil et al., 2013). Meanwhile, the XRD analysis for PPAC-MS presented the peaks at 20° and 60°, matching to magnesium hydroxide (JCPDS file no. 07-0239) and peaks at 36° and 42° assigned as magnesium silicate (JCPDS file no. 07-0230) (Ding et al., 2001; Lin et al., 2015). The XRD patterns for UPPAC and UPPAC-MS obtained after binary mode adsorption were depicted in Fig. 4D. UPPAC-MS had significant sharp peaks at 19.9°, 20.9°, 24.7°, 27.4°, 32.3°, 34.2°, 36.1°, 42.6°, 44.2°, 53.9° and 58.2°, corresponding to hydrocerussite (2PbCO$_3$·Pb(OH)$_2$) (JCPDS file 13-131) (Figueiredo et al., 2006). The results infer that Pb(II) was removed by precipitation on PPAC-MS surface. Whiles, XRD pattern for UPPAC had a similar pattern for PPAC, but all peaks were reduced.

The surface morphologies of PPAC and PPAC-MS were analyzed by FESEM (Fig. 5). PPAC had a smooth surface and consisted of external micropore and mesopore with a honeycomb-like structure (Figs. 5A and 5B). PPAC-MS exhibited a rough surface with some particle

**Fig. 4.** (A) N$_2$ gas adsorption-desorption isotherms of PPAC and PPAC-MS, (B) differential pore volume vs pore width with FASS correction, (C) XRD for PPAC and PPAC-MS, (D) UPPAC and UPPAC-MS in binary mode.
Fig. 5. FESEM and EDS image of (A, B) PPAC, (C, D, E, F) PPAC-MS and (G) element mapping for PPAC-MS.
agglomerate near the pore structure (Fig. 5C). Elemental mapping (Fig. 5D) for PPAC-MS show the Mg and Si were homogeneously dispersed on PPAC surface. As an interesting morphology, PPAC-MS had a thin layer of MgSiO$_3$ without the clogging of external pores (Fig. 5E). With a higher magnification, magnesium silicate exhibited a rough surface like sponge or thin plate mesh-like structure (Fig. 5F). As Gui et al. (2014) reported that magnesium silicate forms petal-like structure under mild hypothermal preparation, this specific morphology might occur by the hydrothermal treatment. The results of EDX (Fig. 5G) and elemental mapping represent that Mg and Si were homogeneously dispersed on the surface and their positions were shown at the similar location. Therefore, it infers that the thin layer is composed of magnesium silicate on PPAC-MS as depicted in Fig. 5G. After binary adsorption, thin sheet-like structured material was formed on the surface of UPPAC-MS (Fig. S2A and S2C in SI). Based elemental mapping and EDX (Fig. S2B and S2D in SI), the thin sheet structure is hydrocerrussite because the Pb and O elements match with the thin sheet structure location.

3.5. Pb(II) adsorption mechanism

Isotherm and kinetic adsorption results indicated that Pb(II) adsorption on PPAC-MS is mainly involved with Si, Mg and hydroxide (OH), because the adsorption capacities for Pb(II) in single mode is similar to those in binary mode. As another evidence, the presence of BPA did not have any effect on the Pb(II) removal by PPAC-MS in binary pollutant mode. In this study, the analytical results of FTIR, FESEM and XRD were utilized to investigate the mechanism of Pb(II) removal by PPAC-MS. Based on the description of previous section, the mechanism of Pb(II) removal can be proposed as precipitation and ion-exchange.

First, Pb(II) can be exchanged with Mg(II) due to the dissolution of Mg(OH)$_2$ from MgSiO$_3$ coated on PPAC-MS. Especially, the negatively charged of Si-O formed on PPAC-MS surface electrostatically attract the positively charged Pb(II). Second, OH$^-$ releases from the dissolution of magnesium hydroxide so that the increase of pH causes the precipitation of Pb(II). The FTIR result indicated the precipitation of Pb(II) as hydrocerrussite [Pb$_3$(CO$_3$)$_2$(OH)$_2$] (Kim and Herrera, 2010). This result was also supported by the result of XRD, specifying that UPPAC-MS presented a XRD pattern of hydrocerrussite in Fig. 4D. Thus, the removal mechanism of Pb(II) by PPAC-MS can be considered as the ion exchange followed by precipitation. As shown in the result of element mapping (Fig. S2B in SI), Pb(II) precipitation was occurred on the top of Pb(II) exchanged silicate because O, Pb and Si were detected at the similar location (Cao et al., 2012). Thus, it can infer that Pb(II) precipitation might occur on the similar locations of ion exchange sites. Along with the result, the FTIR indicated that Si-O-Me bond was found on UPPAC-MS at peak 989 cm$^{-1}$, representing the occurrence of the bond of Pb(II) on Si-O revealed the chemisorptions of Pb(II) onto adsorbent. The surface reaction depicted for the removal mechanism of Pb(II) by PPAC-MS can be shown below.

\[
\text{(PPAC-MS) PPAC-Si-O-Mg-OH + Pb(II) $\leftrightarrow$ AC-Si-O-Pb(OH) + Mg(II) + OH$^-$ (Ion Exchange)}
\]

\[
\text{PPAC-Si-O-Pb(OH) + Pb(OH)$_2$ $\leftrightarrow$ AC-Si-O-Pb-O-Pb(OH)$_3$ (Precipitation)}
\]

Meanwhile, the removal of BPA by PPAC might be happened by OH and carboxylic (COO) groups on PPAC surface. Thus, a decrease in the surface oxygen functional groups of activated carbon reduces the Pb(II) adsorption process. Pb(II) adsorption capacity by PPAC greatly decreased in binary mode and PPAC had similar adsorption capacities of BPA in both single and binary modes. Accordingly, it can be deduced that the oxygen functional group on PPAC surface might be covered by BPA to reduce the removal efficiency of Pb(II) since BPA has a priority in the adsorption surface.

3.6. BPA adsorption mechanism

The intermolecular force such as $\pi-\pi$ interaction could be the dominant mechanism for the adsorption of an organic compound consisting of aromatic or C=C double bond on graphene layer of activated carbon (Bautista-Toledo et al., 2005; Coughlin and Ezra, 1968). Secondly, OH group on activated carbon surface can form a hydrogen bond with BPA (Xu et al., 2012). FTIR results indicated that aromatic C=O and C-O-H bonds were detected on UPPAC and UPPAC-MS after binary adsorption. Thirdly, BPA can be co-precipitated during the precipitation of Pb on the surface of PPAC-MS and PPAC in binary mode. Based on the results of BPA adsorption isotherms and kinetics, BPA adsorption increased with the present of Pb(II). However, PPAC had similar adsorption capacities of BPA in single and binary pollutant mode. Thus, BPA adsorption for PPAC has a priority compared to Pb(II) adsorption. Li et al. presented the adsorption of BPA to sediment increased in the existence of Pb(II) (Li et al., 2007). Sridharan and Lee (1972) found that iron salt can co-precipitate organic compound in lake water. In the result of FTIR (Fig. S1), BPA peaks were found at UPPAC and UPPAC-MS for binary mode. Overall, the mechanisms of BPA removal involved by PPAC-MS and PPAC in binary mode are $\pi-\pi$ intermolecular force, hydrogen bond and co-precipitation.

3.7. Ionic strength effect on PPAC and PPAC-MS in binary modes

Fig. 6A represents the effect of ionic strength on the Pb(II) and BPA removal by PPAC and PPAC-MS. As a result, the adsorption capacity of Pb(II) by PPAC was reduced by 33% while PPAC-MS had 46% reduction at 0.1 M of ionic strength. Therefore, PPAC-MS has a high sensitivity on

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\text{Fig. 6. (A) Ionic strength effect for PPAC and PPAC-MS in binary pollutant and (B) regeneration effect for PPAC-MS in binary pollutant.}
\]
the cationic competition compared to PPAC for Pb(II) removal. Several authors reported a high concentration of Na+ contributes a repulsive force for Pb(II) at outer layer of the adsorbent surface, resulting in the decrease of Pb(II) adsorption capacities (Cybele Morales Futalan et al., 2012; Hayes et al., 1988). On the other hand, the adsorption capacities for BPA by PPAC and PPAC-MS were also significant reduced by 62% and 47%, respectively, at 0.1 M of ionic strength. When the concentration of ionic strength increases, BPA adsorption capacity reduces because of the screening effect between the adsorbent surface and BPA molecules (Bautista et al., 2014). This phenomenon can be also explained by the competition between Na+ and BPA for the available adsorption site on PPAC and PPAC-MS (Xu et al., 2012). Therefore, available sorption sites for BPA were occupied by NaCl causing the reduction of BPA adsorption on PPAC and PPAC-MS.

3.8. Regeneration of Pb(II) and BPA retained PPAC-MS

As shown in Figs. 6B, 5 cycles of adsorption-desorption were conducted to find out the reusability of PPAC-MS in binary mode. PPAC-MS had more than 80% of Pb(II) removal capacities during three cycles, but reduced to 65% at 5th cycle. Ou et al. reported that magnetite –magnesium silicate had about 70% of Pb(II) adsorption capacities for first 3 cycles, but reduced to 60% at fifth regeneration cycle using MgII solution as desorption agent. Furthermore, thermal treatment to PPAC-MS had higher than 80% of BPA removal for 5 cycles. Therefore, it can infer that PPAC-MS can be reusable and maintain the sorption capacities using MgII solution and thermal treatment.

4. Conclusion

In this study, PPAC-MS was prepared by a facile hydrothermal treatment. The FESEM-EDX analysis presented that the surface morphology of PPAC-MS had thin plate mesh-like structure, as well as meso- and macropores. The BPA and Pb(II) removal capacities by PPAC-MS and PPMC were compared to conclude that PPAC-MS had more higher efficiencies of Pb(II) and BPA removal, especially in binary mode. Batch adsorption results presented that the co-existence of Pb(II) in solution significantly affected the removal of BPA for PPAC due to the competition between BPA and Pb(II). Overall, PPAC-MS would have a good potential in wastewater treatment, especially in the case of the application of combined pollutants because of high removal capacity and regeneration rate for Pb(II) and BPA. However, the present of NaCl resulted the decrease of Pb(II) and BPA adsorption capacities by PPAC and PPAC-MS. Therefore, various type of ionic strength influence on the adsorption process should be considered in the future. Due to its high sorption capacities and reusability, overall, PPAC-MS has a high potential in the treatment process for wastewater containing toxic heavy metals and emerging contaminants.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2017.10.025.

References


ECOTOXICOLOGY AND ENVIRONMENTAL SAFETY 148 (2018) 142–151
Shekinah, P., et al., 2002. Adsorption of lead(II) from aqueous solution by activated
Spectrosc. 2016, 5.
Xu, J., et al., 2012. Decontamination of bisphenol A from aqueous solution by graphene
adsorption. Langmuir 28, 8418–8425.
Yakout, S.M., Borai, E.H., 2014. Adsorption behavior of cadmium onto natural chabazite:
batch and column investigations. Desalin. Water Treat. 52, 4212–4222.
Yang, Y., et al., 2013. Preparation of reduced graphene oxide/poly(acrylamide) nano-
composite and its adsorption of Pb(II) and methylene Blue. Langmuir 29, 10727–10736.
Yousefi, M., 2014. A fast method for synthesis magnesium hydroxide nanoparticles,
4, 383–388.