Highly Efficient Lead Distribution by Magnetic Sewage Sludge Biochar: Sorption Mechanisms and Bench Applications

Jerosha Ifthikar ^a, Jia Wang ^b, Qiliang Wang ^b, Ting Wang ^a, Huabin Wang ^b, Aimal Khan ^a, Ali Jawad ^{a,b}, Tingting Sun ^a, Xiang Jiao ^a, Zhuqi Chen ^{a*}

^a Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, P. R. China;

^b Department of Environmental Engineering, School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, P. R. China;

* Corresponding author: Tel: +86 27 87792151; fax: +86 27 87792151

E-mail address: zqchen@hust.edu.cn (Zhuqi Chen^{*}).

Abstract

Highly efficient magnetic sewage sludge biochar (MSSBC) discloses feasible fabrication process with lower production cost, superior adsorption capacity, usage of waste sewage sludge as resource, selected by external magnetic field and exceptional regeneration property. 2 g L⁻¹ MSSBC exhibited a high adsorption capacity of 249.00 mg g⁻¹ in 200 ppm Pb(II) and the lead-MSSBC equilibrium was achieved within one hour, owing to the existence of the copious active sites. The adsorption kinetics was well described by the pseudo-second-order model while the adsorption isotherm could be fitted by Langmuir model. Mechanism study demonstrated the adsorption involved electrostatic attraction, ion exchange, inner-sphere complexation and formation of co-precipitates at the surface of MSSBC. Additionally,

adsorption performance maintained remarkable in a broad pH window. These outcomes demonstrated the promising waste resource utilization by a feasible approach that turns the solid waste of sewage sludge into biochar adsorbent with auspicious applications in elimination of Pb(II) from wastewater.

Keywords:

Lead removal; Sewage sludge; Biochar; Magnetic separation; Adsorption.

1. Introduction

Heavy metal contamination of water and soil is a solemn challenge worldwide, that intensively demands immediate remediation because of its non-degradable ability and toxicity (Ju et al., 2009). Among various heavy metals, lead ions can be commonly found in various industrial wastewater (Al Omar et al., 2016). Lead is known as human carcinogen and which can cause brain impairment, kidney failure, hypertension, damage in nervous system and anaemia (Griswold and Martin et al., 2009). Thus, the United States Environmental Protection Agency (US EPA) mandates the maximum contaminant level (MCL) for lead ions in drinking water at 0.015 ppm (Griswold and Martin et al., 2009).

Thus far, numerous technologies applied over the years for lead elimination, such as phytoremediation (Ali et al., 2013), chemical precipitation (Haddou et al., 2014), membrane separation (Hajdu et al., 2012), flocculation (Pang et al., 2011), ion exchange (Ahmed et al., 1998), redox (Vetrisevi and Jaya Santhi, 2015) and adsorption (Goel et al., 2005). Among them, adsorption is a general technology to effectively remove heavy metal ions, thus diverse materials have been designed and conducted as adsorbents to eliminate heavy metal ions from wastewater in both academic research and industrial application. Conventional adsorbents such as activated carbon (Goel et al., 2005; Largitte et al., 2014), natural clay (Sdiri et al., 2016), and unmodified chitosan (Liu et al., 2013) commonly have low adsorption capacity and weak binding affinity for lead. Initially, various modifications or activation technologies were conducted to improve their performance in environmental remediation. For instance, treated activated carbon (Goel et al., 2005), magnetic chitosan (Gutha and Munagapati, 2016), manganese oxide-coated carbon nanotube (Wang et al., 2007), pretreated clinoptilolite (Günay et al., 2007) were synthesized and investigated. Although versatile adsorbents have proven to hold the weighty increase in capacity with shorter equilibrium time

for removal of lead than conventional adsorbents, the dilemma still remains between cumbersome steps in modifications and economical demand of low cost. This cumbersome synthetic steps and high cost for fabrication limits the application of these novel adsorbents in the industrial scale. Therefore, effective adsorbents fabricated with simple method through less economy and feasible feedstock is still in great demand for heavy metal removal.

Biochar is black carbon which is the pyrolytic product of biomass under oxygen-limited condition. It is an effective adsorbent (Tan et al., 2015) which comprises of high specific surface area, porous structure, inorganic components and various surface active sites (Zhang et al., 2015). Due to the abundant feedstock and simple preparation method, biochar has been widely applied as an adsorbent with acceptable low cost. On the other hand, Sewage sludge is a sort of waste biomass residue that comes out from wastewater treatment by biological processes (Zhai et al., 2012), and is comprised of organic compounds, macro- and micronutrients, trace elements, micro-organisms and micro pollutants (Yuan et al., 2013). Thus, sewage sludge can be considered as a promising feedstock for biochar with tremendous amount. Recently, the amount of sewage sludge kept rising rapidly (Tan et al., 2014), and the treatment of sewage sludge in an economically and environmentally tolerable manner has become one of the most serious problem confronting the society today. Therefore, transformation of sewage sludge into biochar can partly offset the need to install conventional sewage-treatment infrastructure. Pristine biochars, which was prepared from sewage sludge, have been firstly testified for removal of lead (Lu et al., 2012), but achieved capacity is still unsatisfactory. On the other hand, it is challenging to isolate powdered biochar from the aqueous solution due to the small size of particles. A system which can capture the heavy metal ions with great competence and then to isolate them out with ease is essential. Therefore, imprinting magnetite nanoparticles (iron oxide) into pristine biochar to prepare magnetic biochar is recognized as a promising strategy (Wang et al., 2015; Yan et al., 2015).

In literature, many efforts have been paid to remove heavy metal ions from aqueous solution by magnetic biochars, which are fabricated from various biomass. For example, magnetic biochar from agricultural biomass, magnetic oak wood and oak bark fast pyrolysis biochars applied to eliminate lead and cadmium from wastewater (Yap et al., 2017) (Mohan et al., 2014), magnetic biochar prepared with *Astragalus membranaceus* residue used to remove chromium ions (Shang et al., 2016), arsenic(V) removal performed by magnetic gelatin modified biochar (Zhou et al., 2017). Until now, the application of sewage sludge biochar modifications remains limited.

To overcome the aforesaid challenges, we prepared highly effective sewage sludge biochar (SSBC) and magnetic sewage sludge biochar (MSSBC) for elimination of lead ions in aqueous solution. The MSSBC was synthesized employing zinc chloride as fabricating pore agent. The adsorption property of these materials for Pb(II) removal in aqueous solution was evaluated by exploring sorption kinetics and isotherms and testifying the influence of significant parameters such as dosages and pHs on the sorption. Mechanism insights from the characterization of zeta potential, elemental analysis, FTIR, XRD, SEM-EDX, BET suggest that above adsorption behaviour of MSSBC is originated from the existence of copious active sites on the surface and multiple interactions between Pb(II) and MSSBC. Finally, the lead loaded MSSBC can be easily isolated from the aqueous solution by a permanent magnet after adsorption and MSSBC can be easily regenerated and recycled.

2. Materials and methods

2.1. Materials

Zinc chloride (98%) was obtained from J&K Chemical Ltd. (Shanghai, China). Iron(III) chloride hexahydrate ($\geq 99.0\%$), iron(II) sulphate heptahydrate ($\geq 99.0\%$), lead nitrate ($\geq 99.0\%$), hydrochloric acid (36.0~38.0%) and Na₂EDTA ($\geq 99.0\%$) were provided by

Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium hydroxide (96%) was purchased from Tianli Chemical Reagent Co. Ltd. (Tianjin, China). All reagents used in the experiment were of analytical reagent and solutions were prepared with high purity water. Dewatered sewage sludge was obtained from Tangxun Lake Municipal Wastewater Treatment Plant in Wuhan, China. The pristine biochar was made from dried sewage sludge through slow pyrolysis at 400 °C for 2 hours in a furnace tube under an atmosphere of N₂. The attained SSBC was crushed to pass through a 0.3 mm sieve without further modification.

2.2. Fabrication of magnetic sewage sludge biochar

The MSSBC was fabricated according to following procedures. The SSBC was soaked with zinc chloride (Kong et al., 2014)(Khalili et al., 2000) (ZnCl_2 : SSBC = 2:1, weight:weight) and the mixture was heated at 700 °C for 2 h. Then the heated SSBC product was washed with 0.1 mol L⁻¹ HCl followed by deionized water several times, since the pH was 6.0 - 6.5. Then the product was dried and sieved mesh with less than 0.45 mm, which was applied for magnetization. Thus treated SSBC (20 g) was suspended in a 200 mL of deionized water. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (20 g) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (11.1 g) was dissolved in 600 mL deionized water. These two solutions were mixed and stirred at room temperature (20 – 25 °C) for 20 min. Thereafter 10 M NaOH solution was added dropwise into the mixed suspension until the pH was 10 – 11 and stirred for 1 h, the mixture was set aside for one day and filtered. At the end, the filtrate was splashed with deionized water and ethanol several times and dried at 70 °C for 12 h in a hot air oven. The prepared MSSBC was grounded to pass through a 0.45 mm mesh.

2.3. Characterizations

The elemental composition (C, H, N and S) of SSBS and MSSBC were detected by a Vario MICRO cube elemental analyser (German). FTIR spectra were measured via VERTEX 70

Fourier transform infrared spectrometer (USA) using the KBr pellet technique, and were examined in the $4000 - 400 \text{ cm}^{-1}$ region. The surface morphologies of the materials were carried out with a Quanta 200 ESEM (FET, Holland). The crystalline structure was characterized via X-ray diffraction spectra with an X'Pert PRO X-ray photoelectron spectrometer (PANalytical B.V, Holland). The Brunauer-Emmett-Teller (BET) surface area, pore width and pore volume of samples were measured by a Micromeritics ASAP 2420 Surface area and porosity analyser (USA). Magnetic property of the MSSBC was determined by magnetization curve using EM4-HVA ELECTROMAGNETIC magnetometer (Lake Shore, USA). The zeta potentials of MSSBC were measured at different pH by Zetasizer Nano series (Nano-ZS90, Malvern, UK).

2.4. Batch sorption equilibrium experiments

MSSBC adsorbent was used to study the dosage effects on lead removal. Batch sorption experiments were carried out by adding 5 – 75 mg of MSSBC to 25 mL of Pb(II) solution (200 ppm) in vials at 25 °C. Effects of pH (2.0 - 6.0) experiments were directed by addition of 50 mg sorbent to 25 mL of Pb(II) solution (200 ppm) in vials at 25 °C. The pH was adjusted to desired values by adding insignificant volumes of 0.01 M NaOH or HNO₃. An adsorption isotherm analysis was carried out by mixing 50 mg of the sorbent with 25 mL of Pb(II) solution at various concentrations in the range of 20 –1000 ppm at 25 °C.

Correspondingly, kinetic experiments were studied by adding 50 mg sorbent to 50 mL of Pb(II) solution (200 ppm) at 25 °C for different time intervals (5, 10, 30, 60 min and 2, 4, 6, 18 h). The vials were closed and shaken in the mechanical shaker for 18 h to attain the adsorption equilibrium state. The desorption of the lead loaded MSSBC was conducted using 0.1 M Na₂EDTA solution as eluent at 25 °C with MSSBC dose of 2 g L^{-1} . The lead loaded MSSBC was shaken in Na₂EDTA solution for 1 hour and rinsed with water for three times. Then the treated MSSBC was applied in the recycle adsorption study. Once the adsorption

experiment was completed, the mixtures were filtered through 0.22 µm pore size nylon filters. The lead concentration of the samples was measured by a microwave plasma – atomic emission spectroscopy (MP-AES 4200, USA). The amount of Pb(II) adsorbed by the sorbent at equilibrium (q_e) was calculated using following equation

$$q_e = (C_o - C_e) V / m$$

where C_o and C_e are initial and equilibrium concentrations of Pb(II) (ppm), respectively, V is volume of Pb(II) solution (L), and m is the mass of adsorbent (g).

3. Results and discussion

3.1. Characterizations

The elemental analysis of SSBC and MSSBC revealed the chemical components and general nature of biochar. Elemental compositions, surface area (S_{BET}) and adsorption capacity for lead were compared between SSBC, MSSBC and various biochars, which were synthesized from different feedstock in literatures. Amongst, SSBC showed a much higher content of sulphur (2.52%) and nitrogen (2.07%) comparing with other biochars (Table 1). For example, only 0.3% ~ 1.36% of nitrogen can be found in various biochar other than SSBC. Meanwhile, the content of sulphur is not available in pine wood biochar and rice husk biochar, whereas 0.04% ~ 0.35% of sulphur can be found in pine bark biochar, oak wood biochar, oak bark biochar and energy cane biochar. The existence of higher content of sulphur and nitrogen was due to the presence of organic compounds, micro-organisms such as bacteria, animal wastes and some other dead organisms in the sewage sludge from wastewater treatment plant, which is significantly distinguished from traditional biochars that prepared from biomass such as woody plants. Higher content of sulphur and nitrogen can contribute to the capacity of adsorbent. Sulphur and nitrogen normally exists in the form of thiol functional groups and

nitrogen atom on the surface. For instance, SSBC with higher content of sulphur and nitrogen showed 44.91 mg g^{-1} capacity, while aforementioned biochar only demonstrated a capacity between 2.40 mg g^{-1} and 13.10 mg g^{-1} . Noticeably, energy cane biochar with 1.36% nitrogen and 0.35% sulphur also showed remarkable capacity (45.70 mg g^{-1}) of lead, which is consistent with the trend that existence of certain amount of sulphur and nitrogen in the biochar is beneficial to the adsorption of heavy metals. This phenomenon is due to the coordination of Pb(II) ions with thiol functional groups and nitrogen atoms, which were hold free electron doublets. Those free electron doublets could coordinate with Pb(II) ions and stabilize on SSBC (Li et al., 2014; Guibal, 2004).

Meanwhile, surface area (S_{BET}) is also critical for the adsorption of heavy metal ions. Pine bark biochar, oak wood biochar, and oak bark biochar display the S_{BET} of 1.88, 2.04 and $25.40 \text{ m}^2 \text{ g}^{-1}$, respectively. Since oak bark biochar has higher S_{BET} than other two, it illustrates a higher adsorption capacity of 13.10 mg g^{-1} for Pb(II) than that of pine bark biochar and oak wood biochar. Furthermore, a larger S_{BET} of SSBC ($40.96 \text{ m}^2 \text{ g}^{-1}$) also leads to its improved capacity than other aforementioned biochars. Pine wood biochar, rice husk biochar, pine bark biochar, oak wood biochar and oak bark biochar show the adsorption capacity of 4.25, 2.40, 3.00, 2.64 and 13.10 mg g^{-1} for Pb(II), respectively, while that of SSBC reaches 44.91 mg g^{-1} . While the fabrication of MSSBC, high temperature (700°C) was applied to SSBC. This process may cause the nitrogen and sulphur to evaporate from MSSBC. Therefore, lower content of nitrogen (0.15%) and sulphur (0.87%) was found in MSSBC comparing with SSBC.

Further investigation of the porous properties on above-mentioned biochars, the surface area (S_{BET}), pore width and pore volume of SSBC, MSSBC were recorded in Table S2. After the magnetic modification, larger S_{BET} of MSSBC ($103.35 \text{ m}^2 \text{ g}^{-1}$) comparing with that of SSBC ($40.96 \text{ m}^2 \text{ g}^{-1}$). Meanwhile, the pore volume of SSBC and MSSBC was calculated to be 0.1164 and $0.2074 \text{ cm}^3 \text{ g}^{-1}$ but the adsorption average pore width was 113.6308 and $80.2742 \text{ \AA}$, respectively, indicating that MSSBC possesses a larger pore volume but smaller pore width than that of SSBC. Zinc chloride was introduced as the fabricating pore agent (Tan et al., 2016) during the preparation of MSSBC, which made micropores and mesopores throughout the whole SSBC structure. As a result of that MSSBC possessed large surface area and pore volume. Smaller pore width can also be attributed to the introduction of zinc chloride and magnetite that occupied certain pore channels of SSBC. These findings partially support the trend in Table 1 that higher surface area of an adsorbent is beneficial to its higher adsorption capacity for lead removal. For instance, MSSBC showed greater adsorption capacity (249.00 mg g^{-1}) for Pb(II) in comparison with SSBC (44.91 mg g^{-1}).

SEM analysis was used to examine the external morphology of the SSBC and MSSBC with different magnifications (Fig. S1). Both SSBC and MSSBC exhibited well developed pore structure, and while comparing the SEM images of SSBC and MSSBC in Fig. S1 (c) and (d) it clearly shows that splendid particles appeared on the surface of MSSBC, which can be attributed to magnetic nanoparticles (Fe_3O_4) (Zhang et al., 2015) formed during the magnetization. However, distinct reduction of pore width on the surface of MSSBC can be observed (Fig. S1 (c), (d)). This phenomenon can be explained by the introducing of amendment of magnetite, which blocked the pore surface of MSSBC. Above mentioned findings were partially consistent with the results of pore distribution properties (Table S2). SEM-EDX analysis was used to determine the weight and atomic percentage of elements at

the surface of SSBC (Fig. S2). It is mainly composed of C, O, Mg, Al, Si, P, Pt, K and Ca because sewage sludge consists of organic compounds, macro- and micronutrients, trace elements, micro-organisms and micro pollutants. The elements such as calcium and magnesium ions were involved in ion exchange with Pb(II) ions during the lead adsorption. Additionally, co-precipitates of silica with lead were formed after the lead adsorption. These are further explained and evidenced in the section of adsorption mechanism.

The FTIR spectra of SSBC and MSSBC were presented in Fig. S3. In the case of SSBC, the adsorption band at the wavenumber of 3427 cm^{-1} was attributed to the stretching vibration of O–H and N–H groups (Zhang et al., 2015), with signals at 1628 cm^{-1} to the stretching vibration of C=C, 1034 cm^{-1} to stretching vibration of C–O and 796 cm^{-1} to aromatic ring C–H correspondingly. Meanwhile, the peaks at 693 cm^{-1} , 534 cm^{-1} and 471 cm^{-1} were categorised as the finger print regions of organic matters (Chen et al., 2015). FTIR spectrum of MSSBC was similar to that of SSBC. The additional peak of MSSBC at 1379 cm^{-1} and 565 cm^{-1} was corresponded to N–O stretching vibration and Fe–O stretching vibration, respectively, which is consistent with the amendment of magnetite at the pristine biochar.

Through the purpose of investigating the crystalline structures, phase purity and composition of SSBC and MSSBC, XRD was conducted and the patterns were shown in Fig S5. Strong and sharp reflection XRD peaks at 20.86° , 36.55° , 50.15° and 59.98° can be indexed to (100), (110), (112) and (121) planes of SiO_2 (Will et al., 1988; Han et al., 2015), which recommended that SiO_2 was identified as the major crystalline phase in SSBC. Besides signals of SiO_2 , which were similar to that of SSBC, five new peaks at 30.06° , 35.32° , 42.94° , 53.36° , 56.97° , and 62.48° were observed in MSSBC. These peaks were corresponding to the (220), (311), (400), (422), (511), and (440) planes of magnetite (Fe_3O_4) (Yan et al., 2015; Han et al., 2015) respectively, which was due to the introduction of

magnetite and zinc chloride during the preparation of adsorbent (Xu et al., 2013) and forming well crystallized magnetite in MSSBC.

The room-temperature magnetization hysteresis curve was measured via vibrating sample magnetometer (VSM) to exhibit the appropriateness of ferromagnetic materials. This was attained from plots of magnetization (M) against the magnetic field (Oe) as presented S-like curve in Fig. S6. The saturation magnetization (Ms) of the MSSBC was calculated as 5.52 emu g⁻¹, which was ample to be separated from aqueous solution by a permanent magnet (Mohan et al., 2007) as shown in Fig. S6 inset.

3.2. Adsorption study

3.2.1 Adsorption Capacity

Adsorbent dosage is a significant impact factor of adsorption process. It determines the adsorbent-adsorbate equilibrium of the system (Tan et al., 2015). The elimination percentage of Pb(II) was increased from 25% to 100% as the dosage was raised from 0.005 g to 0.050 g, and remained at nearly 100% when the dosage touched 0.075 g. On the other hand, the maximum capacity of 249.00 mg g⁻¹ was achieved at the dosage of 0.005 g and decreased with the increasing dosage of adsorbent (Fig. 1). MSSBC is demonstrated with superior capacity to remove the Pb(II) ions from wastewater comparing with various magnetic modified biochar adsorbents in literatures (Table 2). This remarkable performance is owing to the existence of the copious active sites as evidenced above, and multiple interactions between Pb(II) and MSSBC such as electrostatic attraction, ion exchange, complexation and co-precipitation.

3.2.2 Effect of pH

The initial solution pH offers significant influence in sorption process. The removal of Pb(II) by MSSBC under different initial solution pH were shown in Fig. S7. From this illustration, the removal efficiency of Pb(II) increased with the increasing of pH from 2.0 to 4.0, and maintained at 100% in the broad pH range from 4.0 to 6.0. The pH dependence of Pb(II) was mostly associated with the surface charge of the adsorbent at different pH environment. Above findings were consistent with zeta potential analysis of MSSBC at different solution pHs in Fig. S8. The zero point of zeta potential (pH_{ZPC}) of MSSBC was determined as 2.4. When the solution pH was 2.0, which was lower than pH_{ZPC} of MSSBC, the surface of MSSBC was protonated and electropositive as is evident from the fact that zeta potential of MSSBC at pH 2.0 was 11.15 mV. Electropositive property of MSSBC created electrostatic repulsion between the sorbent surface sites and the cationic Pb(II) ions. However, at pH 3.0 - 6.0 ($>pH_{ZPC}$), the surface of MSSBC was deprotonated and formed electronegative potential. This electronegative property of MSSBC was evidenced by zeta potential analysis, the values were determined as -39.5, -42.8 and -36.8 mV at pH 3.7, 6.0 and 8.8, respectively. Thus strong electrostatic attraction that originated from electronegative sorbent surface and cationic Pb(II) ions led to a higher removal of Pb(II) ions at pH 3.0 - 6.0 compared with the case of electropositive MSSBC at pH 2.0.

3.2.3 Sorption kinetics

The adsorption kinetics of MSSBC on Pb(II) elimination was revealed in Fig. 2. The plots represent the amount of Pb(II) adsorbed (q_t) on MSSBC versus contact time. It is noteworthy that the adsorption of Pb(II) was markedly grasped around 50% within 5 min, This initial stage can be attributed to electrostatic attraction and ion exchange, the process of which was commonly considered to reach equilibrium in a few minutes (Zhang and Lo, 2006). The experimental evidence of electrostatic attraction and ion exchange will be listed in the section

of adsorption mechanism. To further study the process of adsorption, kinetic models were employed to describe the kinetic data. In this investigation, two varied models were employed and exemplified as follows:

The pseudo-first-order model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1.1)$$

The pseudo-second-order model:

$$t/q_t = 1/k_2 q_e^2 + (1/q_e) t \quad (1.2)$$

where q_e and q_t is the amount of Pb^{2+} adsorbed onto MSSBC ($mg\ g^{-1}$) at equilibrium and at time t , respectively. k_1 is the pseudo-first-order rate constant (min^{-1}) and k_2 is the pseudo-second-order rate constant ($g/mg\ min^{-1}$).

The kinetic parameters calculated from the two models were listed in Table 3. Evidently, the plots of t/q_t versus t indicated good linearity in the pseudo-second-order model (Fig. 2 inset).

The correlation coefficient ($R^2\ 0.9976$) of the pseudo-second-order model was higher than that of the pseudo-first-order model ($R^2\ 0.9701$). Moreover, the calculated q_e in Pseudo-second-order ($187.27\ mg\ g^{-1}$) model roughly fitted the experimental data ($249.00\ mg\ g^{-1}$).

Alternatively, q_e value in pseudo-first-order model ($80.07\ mg\ g^{-1}$) was obviously far from the experimental value. Therefore, kinetic data for the adsorption process highly suggested the pseudo-second-order model, which assumed that chemical adsorption of the adsorbate on the adsorbent is dominant (Roberts et al., 1999). In literature, the rate-determining steps of chemical adsorption mainly involved inner-sphere complexation and co-precipitation (Roberts et al., 1999). In our case, the experimental evidence of inner-sphere complexation and co-precipitation was also found and will be illustrated in the mechanism section part 3.4.

3.2.4 Sorption isotherm

Besides adsorption kinetics, the adsorption mechanism was further investigated via absorption isotherms of Pb(II) on MSSBC composite (Fig. 3). As revealed, the adsorption capacities (Q_e) increased along with the increased initial concentration (C_e) and finally got hold of a plateau, demonstrating the maximum adsorption capacity. Two illustrative adsorption models, Langmuir and Freundlich models, were adopted to pretend the sorption isotherm of Pb(II) on MSSBC.

A basic assumption of the Langmuir model is that the adsorption path was monolayer sorption on a homogeneous sorption surface, and all the sorption sites with equivalent sorption energy but without mutual interactions between adsorbed molecules. The Langmuir model can be established to the following linear form based on this assumption (Yan et al., 2015; Li et al., 2010),

$$C_e/Q_e = C_e/Q_m + 1/Q_m K_L \quad (2.1)$$

where Q_e is the adsorption capacity of Pb(II) on sorbent (mg g^{-1}), C_e is the Pb(II) equilibrium concentration in solution (mg L^{-1}), Q_m and K_L represent the maximum adsorption capacity of Pb(II) and the adsorption intensity or Langmuir coefficient (L mg^{-1}), respectively. A plot of C_e/Q_e is plotted against C_e , yielding a straight line with slope of $1/Q_m$ and intercept of $1/Q_m K_L$ (Fig. 3 inset).

The assumption of an exponentially decaying sorption site energy distribution was derived by Freundlich isotherm model. This experimental model can be functional to nonideal sorption on heterogeneous surfaces as well as multilayer sorption. The Freundlich model was expressed by the resulting linear model (Motsa et al., 2011),

$$\log Q_e = \log K_F + 1/n \log C_e \quad (2.2)$$

whereas K_F and n is Freundlich adsorption capacity (mg g^{-1}) and adsorption intensity, respectively. The slope $1/n$ and intercept $\log K_F$ of straight portion of the linear plot was

obtained from plotting $\log Q_e$ versus $\log C_e$. Above-mentioned parameters for Pb(II) adsorption on MSSBC in Langmuir and Freundlich isotherm models were calculated and listed in Table 3.

The Freundlich adsorption intensity parameter n was 1.0502. K_F was 1.6587 mg g^{-1} , which is far lower than that of experimental capacity. Q_m was 241.55 mg g^{-1} from Langmuir isotherm, which is highly consistent with experimental data of 249.00 mg g^{-1} . Although the correlation coefficient (R^2 0.9774) of the Langmuir isotherm is lower than that of the Freundlich isotherm (0.9950). Nevertheless, these two values were in the adequate range (>0.97). Langmuir isotherm can be used to appraise the Pb(II) maximum adsorption capacity of MSSBC. The outcomes reveal that MSSBC has high Pb(II) adsorption capacity of 249.00 mg g^{-1} and adsorption process predominantly depends on homogeneous surfaces along with monolayer sorption. This is also consistent with kinetics data that chemical adsorption plays the dominant role between surface of MSSBC with Pb(II) ions. On the other hand, the chemical adsorption of Pb(II) onto MSSBC creates positive net charge on the surface of MSSBC, if another Pb(II) from wastewater is in contact with MSSBC surface of positive charge then repulsion is possible. Therefore, it is not probable to fit multilayer adsorption of heavy metal ions in Freundlich mode.

Generally, direct comparison among various magnetic biochar is hard due to the specific experimental conditions, thus the performance of adsorbent is normally evaluated through $Q_{\max}$ value from both experimental data and isothermal calculation. As listed in Table 2, among diverse magnetic biochars for Pb(II) removal, MSSBC showed a high adsorption capacity of 249.00 mg g^{-1} within one hour by 2 g L^{-1} dosage. The original of this remarkable performance is speculated from the multiple interaction between MSSBC and Pb(II) ions, which will be further explained in the following mechanism section. The multiple interaction is also consistent with aforementioned kinetics and isothermal results.

3.3. Recycle and Desorption Performance.

To investigate the recoverable potential of MSSBC, 0.1 M Na₂EDTA was applied as eluent and Pb(II) removal efficiency remained >70% after the fifth recycle and desorption efficiency of each cycle was evaluated at about >90%, as shown in Fig. 4. However, it was observed that after five cycles of adsorption-desorption process, the Pb(II) adsorption efficiency only dropped 26.2% compared to the first cycle, indicating a good regeneration and reusability. Furthermore, the presence of magnetic property helps the separation process conveniently and significantly reduces the loss of adsorbent with repetitive usage. Therefore, the advantage of magnetic property with excellent reusability for the efficient removal of Pb(II) ions makes MSSBC as a good potential candidate in wastewater treatment.

3.4. Adsorption Mechanism

The adsorption mechanism of Pb(II) onto MSSBC could be described by both physical and chemical adsorptions. The high surface areas and pore structure of MSSBC, evidenced from BET and SEM, definitely enable them easily accessible to Pb(II) ions and contribute to physical adsorption at the surface (Khare and Goyal, 2013). Meanwhile, the influence of pH and the zeta potential measurement demonstrated the electrostatic attraction between MSSBC and Pb(II) ions. On the other hand, the removal capacity of heavy metal ions is suggested as mainly depending on chemical adsorption rather than physical adsorption (Ding et al., 2014). According to our kinetics experiment, initial fast stage can be attributed to electrostatic attraction and ion exchange, and chemical adsorption is dominant as the rate-determining step. This rate-determining step of chemical adsorption may involve inner-sphere complexation and co-precipitation. Meanwhile, isothermal study demonstrated an adsorption process on homogeneous surfaces along with monolayer chemical sorption. However, the

experimental evidence for the above interactions such as ion exchange, complexation and co-precipitation has not been illustrated yet. Solid evidence for the detailed interaction between the active sites of MSSBC and lead ions may help further understanding on the significant adsorption performance, and will be suggestive to the further improvement of adsorbent. The early stage of absorption on MSSBC is rapid from the view of kinetics. This phenomenon can be attributed to electrostatic attraction and ion exchange. The process is measured to attain equilibrium in a few minutes (Zhang and Lo, 2006). Electrostatic attraction was convincingly demonstrated by the aforementioned zeta potential analysis of MSSBC (Fig. S8). The ions exchanged between Pb(II) and Ca(II)/Mg(II) ions on MSSBC were illustrated by the quantitative analysis on the concentration of Ca(II), Mg(II) ions during adsorption. 0.035 mg Ca²⁺/ 1 g MSSBC and 0.680 mg Mg²⁺/ 1 g MSSBC can be detected by AES after the adsorption of Pb(II), while in the control experiment none of these two ions can be detected after being immersed in aqueous solution in the absence of Pb(II). These verdicts suggest that Pb(II) ions were adsorbed on MSSBC by the process of ion exchange of Ca(II)/Mg(II) ions through reaction 3.1 and 3.2. (Lu et al., 2012).

Fig. S4 (a), (b) revealed FTIR spectra of SSBC, MSSBC before and after adsorption of Pb(II) from aqueous solution. After adsorption of Pb(II), significant shifts from 3427 cm⁻¹ (O-H and N-H) to 3432 cm⁻¹ and 1628 cm⁻¹ (C=C) to 1626 cm⁻¹ were exhibited for SSBC. In the case of MSSBC, characteristic bands changed from 3435 cm⁻¹ (O-H) to 3413 cm⁻¹, 1636 cm⁻¹ (C=O) to 1625 cm⁻¹, 1379 cm⁻¹ (N-O) to 1411 cm⁻¹, and 1104 cm⁻¹ (C-O) to 1097 cm⁻¹. Free carboxyl, sulphur, nitrogen functional groups on MSSBC coordinated with Pb(II) ions by electrostatic surface complexation (Ding et al., 2014). These findings also consistent with the wavelength changes in FTIR band from 1636 cm⁻¹ (C=O) to 1625 cm⁻¹, 1379 cm⁻¹ (N-O) to

1411 cm⁻¹, 1104 cm⁻¹ (C-O) to 1097 cm⁻¹. Further, lead ions bonded with free hydroxyl (O-H) functional groups by way of inner-sphere complexation (Lu et al., 2012), which was suggested by wavelength change in FTIR band from 3435 cm⁻¹ (O-H) to 3413 cm⁻¹. Another important issue that decided the capacity and stability of the adsorbent is the transformation of Pb(II) ions during adsorption. In the case of MSSBC, characteristic XRD patterns of PbO· SiO₂· xH₂O and PbSO₄ co-precipitates were identified by XRD analysis with the typical 2 theta degree of 10.51, 20.87, 27.87, 31.70, 49.12 and 23.15, 29.75, 44.11, 62.09, respectively (Fig. S9). The formation of PbO· SiO₂· xH₂O and PbSO₄ may be due to the reactions with Pb(II) and silica and sulphate on MSSBC, as the amounts of silica were found abundant in the MSSBC and evidenced by SEM-EDX (Fig. S2) and XRD analysis (Fig. S5) and further reveal by reaction 3.3 and 3.4.

As a result, lead adsorption processes on MSSBC involved in electrostatic attraction, ion exchange, electrostatic surface complexation, inner-sphere complexation and co-precipitation. Initial fast stage can be attributed to electrostatic attraction and ion exchange, while the rate-determining steps of chemical adsorption mainly involved inner-sphere complexation and co-precipitation. As evidenced in characterization section, MSSBC showed typical porous structure with large surface area. This property offered tremendous active sites. Together with multiple interactions, MSSBC could be reflected as superior adsorbent to remove Pb(II) ions from wastewater.

4. Conclusion

MSSBC has been proved with feasible synthetic process with low cost, remarkable adsorption capacity with fast equilibrium, minimization of waste sewage sludge, excellent recyclability followed by magnetic separation, and consistent performance under different pHs. Adsorption kinetics was well described by the pseudo-second-order model, and adsorption isotherm could be fitted by the Langmuir isotherm. Initial fast stage of lead adsorption process on MSSBC can be attributed to electrostatic attraction and ion exchange, while the rate-determining steps of chemical adsorption mainly dominated by inner-sphere complexation and co-precipitation. These multiple interactions (Fig. 5) and typical porous structure with large surface area and tremendous active sites on MSSBC contribute to superior performances in Pb(II) removal.

Acknowledgement

This project was funded by National Science Foundation of China [grant number 21671072] and Chutian Scholar Foundation from Hubei province. The authors also thank the Analytical and Testing Center of Huazhong University of Science and Technology for SEM-EDX, FTIR, XRD, BET and elemental analysis.

Supplementary data

Supplementary data to this article can be found online.

References

1. Ahmed, S., Chughtai, S., Keane, M.A., 1998. The removal of cadmium and lead from aqueous solution by ion exchange with Na-Y zeolite. *Separation and Purification Technology* 13, 57–64. doi:10.1016/S1383-5866(97)00063-4

2. Ali, H., Khan, E., Sajad, M.A., 2013. Phytoremediation of heavy metals-Concepts and applications. *Chemosphere* 91, 869–881. doi:10.1016/j.chemosphere.2013.01.075
3. AlOmar, M.K., Alsaadi, M.A., Hayyan, M., Akib, S., Ibrahim, R.K., Hashim, M.A., 2016. Lead removal from water by choline chloride based deep eutectic solvents functionalized carbon nanotubes. *Journal of Molecular Liquids* 222, 883–894. doi:10.1016/j.molliq.2016.07.074
4. Chen, T., Zhou, Z., Xu, S., Wang, H., Lu, W., 2015. Adsorption behavior comparison of trivalent and hexavalent chromium on biochar derived from municipal sludge. *Bioresource Technology* 190, 388–394. doi:10.1016/j.biortech.2015.04.115
5. Ding, W., Dong, X., Ime, I.M., Gao, B., Ma, L.Q., 2014. Pyrolytic temperatures impact lead sorption mechanisms by bagasse biochars. *Chemosphere* 105, 68–74. doi:10.1016/j.chemosphere.2013.12.042
6. Goel, J., Kadirvelu, K., Rajagopal, C., Garg, V.K., 2005. Removal of lead(II) by adsorption using treated granular activated carbon: Batch and column studies. *Journal of Hazardous Materials* 125, 211–220. doi:10.1016/j.jhazmat.2005.05.032
7. Griswold, W., Martin, S., 2009. Human Health Effects of Heavy Metals. *Environmental Science and Technology* 1–6.
8. Guibal, E., 2004. Interactions of metal ions with chitosan-based sorbents: A review. *Separation and Purification Technology* 38, 43–74. doi:10.1016/j.seppur.2003.10.004
9. Günay, A., Arslankaya, E., Tosun, I., 2007. Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics. *Journal of Hazardous Materials* 146, 362–371. doi:10.1016/j.jhazmat.2006.12.034
10. Gutha, Y., Munagapati, V.S., 2016. Removal of Pb(II) ions by using magnetic

- chitosan-4-((pyridin-2-ylimino)methyl)benzaldehyde Schiff's base. *International Journal of Biological Macromolecules* 93, 408–417.
doi:10.1016/j.ijbiomac.2016.08.084
11. Haddou, N., Ghezzar, M.R., Abdelmalek, F., Ognier, S., Martel, M., Addou, A., 2014. Plasmacatalytic removal of lead acetate assisted by precipitation. *Chemosphere* 107, 304–310. doi:10.1016/j.chemosphere.2013.12.071
 12. Hajdu, I., Bodnára, M., Csikósa, Z., Wei, S., Daróczic, L., Kovácsd, B., Gyori, Z., Tamásb, J., Borbély, J., 2012. Combined nano-membrane technology for removal of lead ions. *Journal of Membrane Science* 409–410, 44–53.
doi:10.1016/j.memsci.2012.03.011
 13. Han, Z., Sani, B., Mroziak, W., Obst, M., Beckingham, B., Karapanagioti, H.K., Werner, D., 2015. Magnetite impregnation effects on the sorbent properties of activated carbons and biochars. *Water Research* 70, 394–403.
doi:10.1016/j.watres.2014.12.016
 14. Harikishore, D., Reddy, K., Lee, S.-M., 2014. Magnetic biochar composite: Facile synthesis, characterization, and application for heavy metal removal. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 454, 96–103.
doi:10.1016/j.colsurfa.2014.03.105
 15. Ju, X., Zhang, S., Zhou, M., Xie, R., Yang, L., Chu, L., 2009. Novel heavy-metal adsorption material : ion-recognition P(NIPAM- co -BCAm) hydrogels for removal of lead (II) ions c, 114–118. doi:10.1016/j.jhazmat.2008.12.089
 16. Khalili, N.R., Campbell, M., Sandi, G., Golas, J., 2000. Production of micro- and mesoporous activated carbon from paper mill sludge : I . Effect of zinc chloride activation paper mill sludge. *Carbon* 1905–1915. doi:10.1016/S0008-6223(00)00043-

17. Khare, P., Goyal, D.K., 2013. Effect of high and low rank char on soil quality and carbon sequestration. *Ecological Engineering* 52, 161–166.
doi:10.1016/j.ecoleng.2012.12.101
18. Kong, L., Xiong, Y., Sun, L., Tian, S., Xu, X., Zhao, C., Luo, R., Yang, X., Shih, K., Liu, H., 2014. Sorption performance and mechanism of a sludge-derived char as porous carbon-based hybrid adsorbent for benzene derivatives in aqueous solution. *Journal of Hazardous Materials* 274, 205–211. doi:10.1016/j.jhazmat.2014.04.014
19. Largitte, L., Gervelas, S., Tant, T., Dumesnil, P.C., Hightower, A., Yasami, R., Bercion, Y., Lodewyckx, P., 2014. Removal of lead from aqueous solutions by adsorption with surface precipitation. *Adsorption* 20, 689–700. doi:10.1007/s10450-014-9613-0
20. Li, B., Zhang, Y., Ma, D., Shi, Z., Ma, S., 2014. Mercury nano-trap for effective and efficient removal of mercury(II) from aqueous solution. *Nature communications* 5, 5537. doi:10.1038/ncomms6537
21. Li, Y., Du, Q., Wang, X., Zhang, P., Wang, D., Wang, Z., Xia, Y., 2010. Removal of lead from aqueous solution by activated carbon prepared from *Enteromorpha prolifera* by zinc chloride activation. *Journal of Hazardous Materials* 183, 583–589.
doi:10.1016/j.jhazmat.2010.07.063
22. Liu, B., Lv, X., Meng, X., Yu, G., Wang, D., 2013. Removal of Pb(II) from aqueous solution using dithiocarbamate modified chitosan beads with Pb(II) as imprinted ions. *Chemical Engineering Journal* 220, 412–419. doi:10.1016/j.cej.2013.01.071
23. Liu, Z., Zhang, F.S., 2009. Removal of lead from water using biochars prepared from

- hydrothermal liquefaction of biomass. *Journal of Hazardous Materials* 167, 933–939.
doi:10.1016/j.jhazmat.2009.01.085
24. Lu, H., Zhang, W., Yang, Y., Huang, X., Wang, S., Qiu, R., 2012. Relative distribution of Pb^{2+} sorption mechanisms by sludge-derived biochar. *Water Research* 46, 854–862. doi:10.1016/j.watres.2011.11.058
25. Mohan, D., Kumar, H., Sarswat, A., Alexandre-Franco, M., Pittman, C.U., Mohan, D., 2014. Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars. *Chemical Engineering Journal* 236, 513–528.
doi:10.1016/j.cej.2013.09.057
26. Mohan, D., Pittman, C.U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P.H., Alexandre-Franco, M.F., Gomez-Serrano, V., Gong, H., 2007. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *Journal of Colloid and Interface Science* 310, 57–73.
doi:10.1016/j.jcis.2007.01.020
27. Mohan, D., Singh, P., Sarswat, A., Steele, P.H., Pittman, C.U., 2015. Lead sorptive removal using magnetic and nonmagnetic fast pyrolysis energy cane biochars. *Journal of Colloid and Interface Science* 448, 238–250. doi:10.1016/j.jcis.2014.12.030
28. Motsa, M.M., Mamba, B.B., Thwala, J.M., Msagati, T.A.M., 2011. Preparation, characterization, and application of polypropylene-clinoptilolite composites for the selective adsorption of lead from aqueous media. *Journal of Colloid and Interface Science* 359, 210–219. doi:10.1016/j.jcis.2011.02.067
29. Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 333, 134–139.

30. Pang, F.M., Kumar, P., Teng, T.T., Mohd Omar, A.K., Wasewar, K.L., 2011. Removal of lead, zinc and iron by coagulation-flocculation. *Journal of the Taiwan Institute of Chemical Engineers* 42, 809–815. doi:10.1016/j.jtice.2011.01.009
31. Roberts, D.R., Scheidegger, A.M., Sparks, D.L., 1999. Kinetics of mixed NI-AL precipitate formation on a soil clay fraction. *Environmental Science and Technology* 33, 3749–3754. doi:10.1021/es990235e
32. Sdiri, A., Khairy, M., Bouaziz, S., El-Safty, S., 2016. A natural clayey adsorbent for selective removal of lead from aqueous solutions. *Applied Clay Science* 126, 89–97. doi:10.1016/j.clay.2016.03.003
33. Shang, J., Pi, J., Zong, M., Wang, Y., Li, W., Liao, Q., 2016. Journal of the Taiwan Institute of Chemical Engineers Chromium removal using magnetic biochar derived from herb-residue. *Journal of the Taiwan Institute of Chemical Engineers* 68, 289–294. doi:10.1016/j.jtice.2016.09.012
34. Tan, C., Yaxin, Z., Hongtao, W., Wenjing, L., Zeyu, Z., Yuancheng, Z., Lulu, R., 2014. *Bioresource Technology* Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge. *Bioresource Technology* 164, 47–54. doi:10.1016/j.biortech.2014.04.048
35. Tan, C., Zeyu, Z., Rong, H., Ruihong, M., Hongtao, W., Wenjing, L., 2015. Adsorption of cadmium by biochar derived from municipal sewage sludge: Impact factors and adsorption mechanism. doi:10.1016/j.chemosphere.2015.04.052
36. Tan, X.-F., Liu, Y.-G., Gu, Y.-L., Xu, Y., Zeng, G.-M., Hu, X.-J., Liu, S.-B., Wang, X., Liu, S.-M., Li, J., 2016. Biochar-based nano-composites for the decontamination of wastewater: A review. *Bioresource Technology* 212, 318–333. doi:10.1016/j.biortech.2016.04.093

37. Trakal, L., Veselská, V., Šafařík, I., Vítková, M., Íhalová, S.Č., Komárek, M., 2016. Lead and cadmium sorption mechanisms on magnetically modified biochars. *Bioresource Technology* 203, 318–324. doi:10.1016/j.biortech.2015.12.056
38. Vetriselvi, V., Jaya Santhi, R., 2015. Redox polymer as an adsorbent for the removal of chromium (VI) and lead (II) from the tannery effluents. *Water Resources and Industry* 10, 39–52. doi:10.1016/j.wri.2015.02.003
39. Wang, S. ye, Tang, Y. kui, Chen, C., Wu, J. tao, Huang, Z., Mo, Y. yuan, Zhang, K. xuan, Chen, J. bo, 2015. Regeneration of magnetic biochar derived from eucalyptus leaf residue for lead(II) removal. *Bioresource Technology* 186, 360–364. doi:10.1016/j.biortech.2015.03.139
40. Wang, S.G., Gong, W.X., Liu, X.W., Yao, Y.W., Gao, B.Y., Yue, Q.Y., 2007. Removal of lead(II) from aqueous solution by adsorption onto manganese oxide-coated carbon nanotubes. *Separation and Purification Technology* 58, 17–23. doi:10.1016/j.seppur.2007.07.006
41. Will, G., Bellotto, M., Parrish, W., Hart, M., 1988. Crystal structures of quartz and magnesium germanate by profile analysis of synchrotron-radiation high-resolution powder data. *Journal of Applied Crystallography* 21, 182–191. doi:10.1107/S0021889887011567
42. Xu, X., Cao, X., Zhao, L., 2013. Comparison of rice husk- and dairy manure-derived biochars for simultaneously removing heavy metals from aqueous solutions: Role of mineral components in biochars. *Chemosphere* 92, 955–961. doi:10.1016/j.chemosphere.2013.03.009
43. Yan, L., Kong, L., Qu, Z., Li, L., Shen, G., 2015. Magnetic Biochar Decorated with ZnS Nanocrytals for Pb (II) Removal. *ACS Sustainable Chem. Eng.* 3, 125–132

44. Yap, M.W., Mubarak, N.M., Sahu, J.N., Abdullah, E.C., 2017. Microwave induced synthesis of magnetic biochar from agricultural biomass for removal of lead and cadmium from wastewater. *Journal of Industrial and Engineering Chemistry* 45, 287–295. doi:10.1016/j.jiec.2016.09.036
45. Yuan, H., Lu, T., Zhao, D., Huang, H., Noriyuki, K., Chen, Y., 2013. Influence of temperature on product distribution and biochar properties by municipal sludge pyrolysis. *Journal of Material Cycles and Waste Management* 15, 357–361. doi:10.1007/s10163-013-0126-9
46. Zhai, Y., Peng, W., Zeng, G., Fu, Z., Lan, Y., Chen, H., Wang, C., Fan, X., 2012. Pyrolysis characteristics and kinetics of sewage sludge for different sizes and heating rates. *Journal of Thermal Analysis and Calorimetry* 107, 1015–1022. doi:10.1007/s10973-011-1644-0
47. Zhang, M., Liu, Y., Li, T., Xu, W., Zheng, B., Tan, X., Wang, H., Guo, Y., Guo, F., Wang, S., 2015. Chitosan modification of magnetic biochar produced from *Eichhornia crassipes* for enhanced sorption of Cr(VI) from aqueous solution. *RSC Adv.* 5, 46955–46964. doi:10.1039/C5RA02388B
48. Zhang, W., Lo, I.M.C., 2006. EDTA-enhanced washing for remediation of Pb- and/or Zn-contaminated soils. *Journal of Environmental Engineering* 132, 1282–1288. doi:10.1061/(ASCE)0733-9372(2006)132:10(1282)
49. Zhou, Y., Gao, B., Zimmerman, A.R., Chen, H., Zhang, M., Cao, X., 2014. Bioresource Technology Biochar-supported zerovalent iron for removal of various contaminants from aqueous solutions. *Bioresource Technology* 152, 538–542. doi:10.1016/j.biortech.2013.11.021
50. Zhou, Z., Liu, Y., Liu, S., Liu, H., Zeng, G., Tan, X., Yang, C., Ding, Y., Yan, Z.,

Cai, X., 2017. Sorption performance and mechanisms of arsenic(V) removal by magnetic gelatin-modified biochar. *Chemical Engineering Journal* 314, 223–231. doi:10.1016/j.cej.2016.12.113

Fig. 1. Influence of MSSBC dosage on Pb(II) elimination. Reaction conditions: Initial concentration of Pb(II) 200 ppm at pH 6, 25 mL of solution, 50 mg of adsorbent, 18 hours, 25 ° C. Pb(II) removal percentage and removal capacity versus MSSBC dosage.

Fig. 2. Adsorption kinetic of MSSBC on Pb(II) removal. Symbols are experimental data and solid lines denote the fitted curves. (Inset represents pseudo-second-order (PSO) adsorption kinetics of Pb(II) on MSSBC) Reaction conditions: Initial concentration of Pb(II) 200 ppm at pH 6, 50 mL of solution, 50 mg of adsorbent, 18 hours, 25 ° C.

Fig. 3. Effect of initial concentration of Pb(II) adsorption on MSSBC (Symbols are experimental data and solid lines denote the fitted curves) (Inset represents linear plot of Langmuir isotherm of Pb(II) on MSSBC) reaction conditions: Initial concentration of Pb(II) 20 - 1000 ppm at pH 6, 25 mL of solution, 50 mg of adsorbent, 18 hours, 25 ° C.

Fig. 4. Pb(II) adsorption or desorption efficiencies of MSSBC at five regeneration cycles

Fig. 5. Conceptual sketch of lead adsorption mechanisms on MSSBC

Table 1
Comparison of the maximum adsorption capacity of Pb(II), S_{BET} and elemental compositions on SSBC, MSSBC and various plant pyrolysis biochars.

Biochar	Percentage of existence elements		S _{BET} (m ² g ⁻¹)	Adsorption capacity of Pb(II) (mg g ⁻¹)	Reference
	Nitrogen (%)	Sulphur (%)			
Pine wood biochar	0.30	NA	NA	4.25	(Liu and Zhang, 2009)
Rice husk biochar	0.11	NA	NA	2.40	
Pine bark biochar	0.34	0.04	1.88	3.00	(Mohan et al., 2007)
Oak wood biochar	0.31	0.02	2.04	2.64	(Mohan et al., 2014)
Oak bark biochar	0.46	0.02	25.40	13.10	
Energy cane biochar	1.36	0.35	ND	45.70	(Mohan et al., 2015)
Sewage sludge biochar	2.07	2.52	40.96	44.91	This study
Magnetic sewage sludge biochar	0.15	0.87	103.35	249.00	

Not available (NA), not detectable (ND).

Table 2

Comparison of the maximum uptake of Pb(II) on various magnetic modified biochar adsorbents

Biomass	Modified materials	Adsorption capacity (mg/g)	References
oak wood	Fe ²⁺ /Fe ³⁺ plus SO ₄ ²⁻ solution	10.13	(Mohan et al., 2014)
oak bark	Fe ²⁺ /Fe ³⁺ plus SO ₄ ²⁻ solution	30.20	
energy cane	Ferric sulphate (Fe ₂ (SO ₄) ₃ •nH ₂ O)	40.56	(Mohan et al., 2015)
Bamboo	Fine sized ZVI	25.10	(Zhou et al., 2014)
Pine bark	Ferrite (CoFe ₂ O ₄)	25.30	(Harikishore et al., 2014)
Nut shield	FeSO ₄ •7H ₂ O	179.00	
Grape stalk	FeSO ₄ •7H ₂ O	247.00	(Trakal et al., 2016)
Grape husk	FeSO ₄ •7H ₂ O	204.00	
Plum stone	FeSO ₄ •7H ₂ O	194.00	
Romchar (Harghita, Romania)	Magnetite/maghemite	17.70	(Han et al., 2015)
Oxford Biochar Ltd. (Dorset, UK)	Magnetite/maghemite	32.20	
Rice hull	Fe(acac) ₃ + calcination	23.90	(Yan et al., 2015)
Sewage sludge	Fe ²⁺ /Fe ³⁺ plus SO ₄ ²⁻ solution without ZnCl ₂	99.85	This study
Sewage sludge	Fe ²⁺ /Fe ³⁺ plus SO ₄ ²⁻ solution with ZnCl ₂	249.00	This study

Table 3

Kinetic and Isotherm Model Parameters for Lead Adsorption to the MSSBC.

	Parameter 1	Parameter 2	R^2
Adsorption kinetics			
Pseudo-first-order	$k_1 = 6.2 \times 10^{-3} \text{ min}^{-1}$	$q_e = 80.07 \text{ mg g}^{-1}$	0.9701
Pseudo-second-order	$k_2 = 4.56 \times 10^{-4} \text{ g/mg min}^{-1}$	$q_e = 187.27 \text{ mg g}^{-1}$	0.9976
Adsorption isotherm			
Langmuir	$K_L = 6.78 \times 10^{-3} \text{ L mg}^{-1}$	$Q_m = 241.55 \text{ mg g}^{-1}$	0.9774
Freundlich	$n = 1.0502$	$K_F = 1.66 \text{ mg g}^{-1}$	0.9950