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Adsorption of Pb(II) in Aqueous Solution by the Modified Biochar Derived from Corn Straw with Magnesium Chloride

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ABSTRACT

Lead wastewater not only causes deterioration of water quality but also further enters the human body through the food chain and is harmful to human health. Therefore, there is an urgent need to find an economical, simple and efficient water treatment technology to treat lead-contaminated wastewater in waterbodies. In this paper, the modified biochar derived from corn straw by magnesium chloride is prepared. Adsorption experiments of Pb(II) in solution by the modified biochar are carried out. Experiment results show that the modified biochar mainly contains C and O elements, and a large number of functional groups. The adsorption amount of Pb(II) by modified biochar reaches 5.15 mg/g under 0.2 g of modified biochar, 25 mg/L initial concentration of Pb(II) ion, reaction time of 480 min, temperature 25°C and at a speed of 200 rpm. The adsorption process of Pb(II) ions in solution by the modified biochar fits on the Freundlich isotherm model. Pseudo-second order kinetic model can better describe the adsorption process of Pb(II) ion in solution by the modified biochar. The process of adsorbing Pb(II) ions in solution by modified biochar is dominated by multi-layer adsorption process and chemical adsorption process.

INTRODUCTION

With the widespread application of lead products and lead compounds, lead pollution in the environment has become increasingly serious (Fan et al. 2008, Zhu et al. 2014, Chen et al. 2018). Lead wastewater not only causes deterioration of water quality but also further enters the human body through the food chain and is harmful to human health (Shen et al. 2015, Ho et al. 2017, Shen et al. 2019). Therefore, there is an urgent need to find an economical, simple and efficient water treatment technology to treat lead-contaminated wastewater (Hang et al. 2017, Kwak et al. 2019). At present, the methods for removing Pb(II) ions in solution mainly include chemical precipitation, physical filtration separation, bio-concentration, physical adsorption, and chemical removal (Xiong et al. 2017, Zhang et al. 2019). Among these methods, the adsorption method has become one of the priority methods in practice because of its low cost, high efficiency, and easy operation. It is considered to be one of the most interesting treatment methods in current research (Mohan et al. 2014, Shi et al. 2019). Some adsorbents, such as activated carbon, activated zeolite, resin adsorbent, etc., have the disadvantages of high cost, difficulty in separation, and easy secondary pollution (Shen et al. 2017). Therefore, the development of new, cheap and effective adsorption material has attracted much attention by some researchers (Liu & Zhang 2009, Zhou et al. 2013, Zhou et al. 2017).

Biochar is mainly composed of carbon, hydrogen and oxygen. It is a light carbon material with high carbon content and high aromatization properties (Yahya et al. 2016, Wan et al. 2018, Hang et al. 2019). Therefore, it has a certain adsorption capacity for heavy metals, such as Pb(II) ions, Cu(II) ions, Cr(VI), etc., which affects the distribution, migration and bioavailability of these heavy metals in the environment (Devi & Saroha 2014). However, the adsorption capacity of single biochar for heavy metals is far less than that of a composite modified with other materials (Huang et al. 2015, Huang et al. 2018, Mostafa et al. 2018). The modified biochar by the composite material has the characteristics of low preparation cost, excellent physical and chemical properties, simple operation, good environmental compatibility, etc., and is widely used for the adsorption treatment of heavy metals wastewater (Zhou et al. 2018). The biochar produced by the anoxic pyrolysis of agricultural and forestry waste is a material with developed pore structure, large specific surface area, rich oxygen-containing functional groups and excellent adsorption performance (Mallampati et al. 2012, Mandu et al. 2012, Wang et al. 2015). The yield of the corn stalk in China is huge, which is a common raw material for the preparation of biochar (Yuan et al. 2011).

In this study, the corn straw is chosen as the biomass raw material, which is pyrolyzed under anaerobic conditions to prepare the modified biochar derived from corn straw. Then biochar is modified by the magnesium chloride. The modified biochar by magnesium chloride is obtained. Adsorption experiments of Pb(II) in solution by the modified biochar are carried out in the laboratory. Adsorption kinetics and adsorption isotherms have been discussed in detail.

MATERIALS AND METHODS

Preparation of biochar: The corn straw from the farmland in the suburbs of Jinan city was washed several times with distilled water and dried at 105°C to constant weight. It was then pulverized and passed through a 40 mesh sieve. 20 g of 40-mesh corn straw was pyrolyzed in a muffle furnace at 250°C for 2 hours. The entire operational process was carried out under N_2 gas condition. It was cooled to room temperature, smashed and sieved into 100 mesh to obtain the biochar.

Preparation of the modified biochar by magnesium chloride: 2 g of biochar was taken in a 250 mL Erlenmeyer flask containing 100 mL of 0.01 mol/L magnesium chloride solution and stirred on a magnetic stirrer for 6 hours. It was washed 3 times with distilled water and dried at 105°C to constant weight to obtain the modified biochar by magnesium chloride. The characteristics of biochar were determined by SEM, EDS and FT-IR.

Adsorption experiment: 0.2 g of biochar or 0.2 g of modified biochar was taken in a 250 mL Erlenmeyer flask containing 100 mL of 25 mg/L $Pb(NO_3)_2$ solution. It was shaken for 480 minutes in a constant temperature shaking box at 25°C and a speed of 200 rpm. The sample was filtered through a 0.45 μm filter and determined by atomic absorption spectrometry. Each adsorption test was repeated three times.

Data analysis: The amount of adsorption was calculated by the following formula:

$$q_e = \frac{\left(C_0 - C_e\right) \times V}{m} \quad \ldots(1)$$

Where, q_e (mg/g) is the amount of adsorption per unit mass of adsorbent at the end of adsorption. C_0 (mg/L) and C_e (mg/L) are the initial concentration of the adsorbate in the solution and the concentration at the equilibrium of adsorption. V (mL) is the volume of solution and m (g) is the dosage of the modified biochar.

RESULTS AND DISCUSSION

The characteristics of modified biochar: The SEM image of modified biochar is shown in Fig.1. The surface of the modified biochar is very smooth and some fragments are present. The specific surface area of modified biochar is relatively large, which is favourable for adsorption.

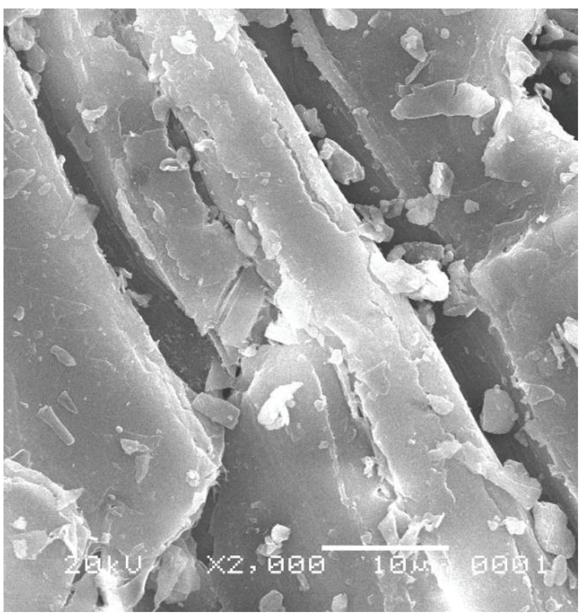

Fig.1: SEM image of modified biochar.

Fig. 2 shows the EDS analysis of biochar. As shown in Fig.2, it implies that modified biochar mainly contains C and O elements, and their contents are 68.85% and 26.68% respectively. This can be thought that the modified biochar is hydrophilic and polar. A small amount of element, such as Mg, Si, S, Cl, K and Ca, is also present on the surface of the modified biochar.

The FT-IR spectra of modified biochar are shown in Fig. 3. It can be concluded that the surface of the modified biochar contains a large number of functional groups. The peak shape is wider between 3100 cm^{-1} and 3600 cm^{-1}, which is -OH stretching vibration (Wang et al. 2008). The peak at 1695 cm^{-1} is the stretching vibration peak of C=O in -COOH functional group. The absorption peak at 1440 cm^{-1} is a C=O stretching vibration (Zhang et al. 2018). The absorption peak at 1228 cm^{-1} is a C-O stretching vibration peak. The peak between 515 cm^{-1} and 735 cm^{-1} is C-H stretching vibration peak (Li et al. 2019). The presence of these functional groups will facilitate the adsorption of pollutant by the modified biochar (Günay et al. 2007).

Adsorption capacity experiment: It can be seen from Fig. 4 that the adsorption capacity of Pb(II) ions in aqueous solution by the modified biochar is significantly enhanced. The adsorption capacity of Pb(II) ions by the modified biochar is more than twice than the unmodified biochar. The adsorption amount of Pb(II) by modified biochar reaches 5.15 mg/g under 0.2 g of modified biochar, 25 mg/L initial concentration of Pb(II) ion, react time of 480 min, temperature 25°C and at a speed of 200 rpm.

Adsorption kinetic: The process of describing the adsorption of solids to liquids is often described by Pseudo-first order kinetic equations and Pseudo-second order kinetic

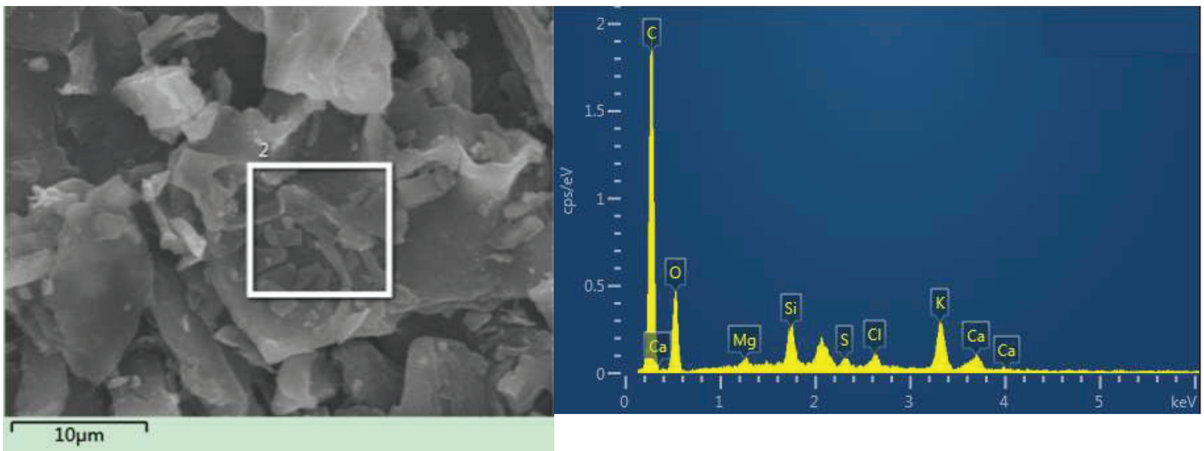

Fig. 2: EDS analysis of modified biochar.

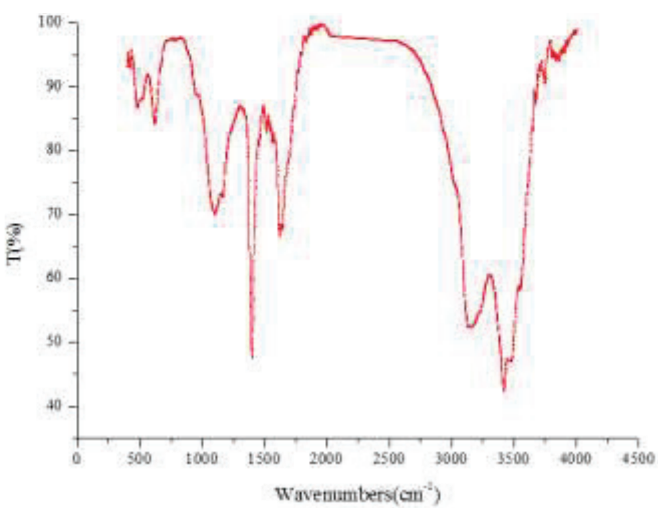

Fig. 3: FT-IR spectra of modified biochar.

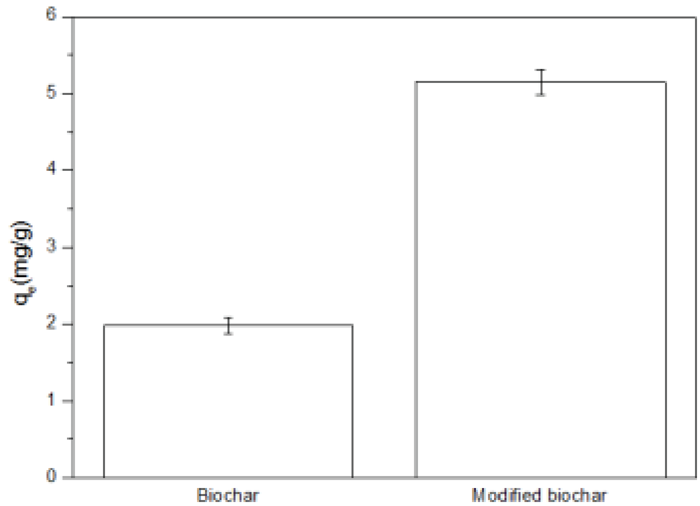

Fig. 4: Adsorption amount of Pb(II) ions in solution by biochar and modified biochar.

equations. Its expression is Eq. 2 and Eq. 3 (Giles et al. 1960).

$$q_t = q_e(1 - e^{-K_1 t}) \quad \ldots(2)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad \ldots(3)$$

Where q_t (mg/g) and q_e (mg/g) are adsorption amount of the adsorbent to the adsorbate at the adsorption time t (min) and the adsorption equilibrium respectively. K_1 (min^{-1}) and K_2 (min^{-1}) are constants.

The adsorption experiments of the contact time influence were carried out according to the following experimental procedure. 0.2 g of modified biochar was taken in a 250 mL Erlenmeyer flask containing 100 mL of 25 mg/L $Pb(NO_3)_2$ solution. The contents were shaken for a serial contact time (5, 10, 15, 30, 45, 60, 120, 240, 360 and 480 min) in a constant temperature at 25°C and a speed of 200 rpm. According to the test results, the fitting equation was performed according to Eq. 2 and Eq. 3. The adsorption kinetic parameters of modified biochar on Pb(II) ions in solution are given in Table 1. According to the value of R^2, the pseudo-second order kinetic model can better describe the adsorption process of modified biochar on Pb(II) ion in solution. Therefore, it can be concluded that the process of adsorbing Pb(II) ions in solution by modified biochar is mainly chemical adsorption.

Adsorption isotherms: In this study, Langmuir isotherm model and Freundlich isotherm model were chosen to describe the adsorption isotherm. Their equations are as below (Liu & Liu 2008, Foroughi-dahr et al. 2015):

$$q_e = \frac{K_L q_{\max}}{1 + K_L C_e} \times C_e \quad \ldots(4)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \ldots(5)$$

Where, C_e (mg/L) is the equilibrium concentration in the solution, q_e (mg/g) is the adsorbate adsorbed at equilibrium, q_{max}(mg/g) is the maximum adsorption capacity, n is the Freundlich constant related to adsorption intensity, K_L (L/mg) and K_F ($(mg/g)^{1/n}$) are the adsorption constants for Langmuir and Freundlich models respectively.

The adsorption experiments of the Pb(II) ions concentration influence were carried out. 0.2 g of modified biochar was taken in a 250 mL Erlenmeyer flask containing 100 mL of a serial of Pb(II) ions concentration (20, 40, 60, 80 and 100 mg/L). They were shaken for 480 minutes in a constant temperature shaking box at 25°C and a speed of 200 rpm. According to the results of the adsorption experiments and Eq. 4 and Eq. 5, parameters of Langmuir isotherm model and Freundlich isotherm model for the description of Pb(II)

Table 1: Kinetics parameters of Pb(II) ions in solution by modified biochar.

Pseudo-first order kinetic model			Pseudo-second order kinetic model		
K_1(min^{-1})	q_e(mg/g)	R^2	K_2(min^{-1})	q_e(mg/g)	R^2
0.03	5.31	0.942	0.09	5.68	0.986

Table 2: Parameters of the Langmuir isotherm model and Freundlich isotherm model for the description of Pb(II) ions in solution adsorption onto modified biochar.

Langmuir			Freundlich		
q_{max}(mg/g)	K_L(L/mg)	R^2	K_F((mg/g)$^{1/n}$)	n	R^2
6.12	0.03	0.747	2.24	0.18	0.982

ions in solution adsorption onto modified biochar are given in Table 2.

From Table 2, Freundlich isotherm model can better describe the adsorption isothermal process of modified biochar on Pb(II) ions in solution according to the value of R^2. The adsorption process is monolayer adsorption process. Therefore, it can be concluded that the process of adsorbing Pb(II) ions in solution by modified biochar is dominated by multi-layer adsorption.

CONCLUSIONS

Based on the above experimental results, the following conclusions can be drawn.

(1) The adsorption ability of Pb(II) ions in solution by the modified biochar is better than that of the unmodified biochar. The surface of the modified biochar is very smooth structure and some fragments are present. It contains a large number of functional groups, such as C=O, C-H, -OH, etc.

(2) The adsorption amount of Pb(II) by modified biochar reaches 5.15 mg/g under 0.2 g of modified biochar, 25 mg/L initial concentration of Pb(II) ion, react time of 480 min, temperature 25°C and a speed of 200 rpm.

(3) Pseudo-second order kinetic model can better describe the adsorption process of modified biochar on Pb(II) ion in solution. The process of modified biochar on Pb(II) ions in solution fits the Freundlich isotherm model.

(4) The process of adsorbing Pb(II) ions in solution by modified biochar is dominated by multi-layer adsorption and chemical adsorption process.

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REFERENCES

Chen, Y.F., Ho, S.H., Wang, D.W., Wei, Z.S., Chang, J.S. and Ren, N.Q. 2018. Lead removal by a magnetic biochar derived from persulfate-ZVI treated sludge together with one-pot pyrolysis. Bioresource Tech., 247: 463-470.

Devi, P. and Saroha, A.K. 2014. Synthesis of the magnetic biochar composites for use as an adsorbent for the removal of pentachlorophenol from the effluent. Bioresource Tech., 169: 525-531.

Fan, T., Liu, Y., Feng, B., Zeng, G., Yang, C., Zhou, M., Zhou, H., Tan, Z. and Wang, X. 2008. Biosorption of cadmium(II), zinc(II) and lead(II) by *Penicillium simplicissimum*: isotherms, kinetics and thermodynamics. J. Hazard. Mater., 160: 655-661.

Foroughi-dahr, M., Abolghasemi, H., Esmaieli, M., Nazari, G. and Rasem, B. 2015. Experimental study on the adsorptive behavior of Congo red in cationic surfactant-modified tea waste. Process Saf. Environ., 95: 226-236.

Giles, C.H., MacEwan, T., Nakhwa, S. and Smith, D. 1960. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. J. Chem. Soc., 6: 3973-3993.

Günay, A., Arslankaya, E. and Tosun, I. 2007. Lead removal from aqueous solution by natural and pretreated clinoptilolite: Adsorption equilibrium and kinetics. J. Hazard. Mater, 146: 362-371.

Hang, Y., Si, Y., Zhou, Q., Yin, H.B., Wang, A.L. and Cao, A.M. 2019. Morphology-controlled synthesis of calcium titanate particles and adsorption kinetics, isotherms, and thermodynamics of Cd(II), Pb(II), and Cu(II) cations. J. Hazard. Mater., 380: 120789-120798.

Hang, Y., Yin, H., Ji, Y., Liu, Y., Lu, Z., Wang, A., Shen, L. and Yin, H.X. 2017. Adsorption performances of naked and 3-aminopropyl triethoxysilane-modified mesoporous TiO_2 hollow nanospheres for Cu^{2+}, Cd^{2+}, Pb^{2+}, and Cr(VI) ions. J. Nanosci. Nanotechnol., 17: 5539-5549.

Ho, S.H., Chen, Y.D., Yang, Z.K., Nagarajan, D., Chang, J.S. and Ren, N.Q. 2017. High-efficiency removal of lead from wastewater by biochar derived from anaerobic digestion sludge. Bioresource Tech., 246: 142-149.

Huang, D.L., Deng, R., Wan, J., Zeng, G.M., Xue, W.J., Wen, X.F., Zhou, C.Y., Hu, L., Liu, X.G., Xu, P., Guo, X.Y. and Ren, X.Y. 2018. Remediation of lead-contaminated sediment by biochar-supported nano-chlorapatite: Accompanied with the change of available phosphorus and organic matters. J. Hazard. Mater., 348: 109-116.

Huang, X., Liu, Y., Liu, S., Tan, X., Ding, Y., Zeng, G., Zhou, Y., Zhang, M., Wang, S. and Zheng, B. 2015. Effective removal of Cr(VI) using βcyclodextrin-chitosan modified biochars with adsorption/reduction bifunctional roles. RSC Adv., 6: 94-104.

Kwak, J.H., Islam, M.S., Wang, S.Y., Selamawit, A.M., Naeth, M.A., Mohamed, G.E. and Scott X.C. 2019. Biochar properties and lead(II) adsorption capacity depend on feedstock type, pyrolysis temperature, and steam activation. Chemosphere, 231: 393-404.

Li, J.H., Zheng, L.R., Wang, S.L., Wu, Z.P., Wu, W.D., Nabeel, K.N., Sabry, M.S., Jörg, R., Bolan, N., Yong, S. and Wang, H.L. 2019. Sorption mechanisms of lead on silicon-rich biochar in aqueous solution: Spectroscopic investigation. Sci. Total Environ., 672: 572-582.

Liu, Y. and Liu, Y.J. 2008. Biosorption isotherms, kinetics and thermodynamics. Sep. Purif. Tech., 61: 229-242.

Liu, Z.G. and Zhang, F.S. 2009. Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. J. Hazard. Mater., 167 (1-3): 933-939.

Mallampati, S.R., Mitoma, Y., Okuda, T., Sakita, S. and Kakeda, M. 2012. Enhanced heavy metal immobilization in soil by grinding with addition of nanometallic Ca/CaO dispersion mixture. Chemosphere, 89: 717-723.

Mandu, I., Gao, B., Yao, Y., Xue, Y.W., Zimmerman, A., Pratap, P. and Cao, X.D. 2012. Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass. Bioresource Tech., 110: 50-56.

Mohan, D., Kumar, H., Sarswat, A. and Alexandre, F.M. 2014. Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis biochars. Chem. Eng. J., 236: 513-528.

Mostafa, F.E., Ahmed, M., Gao, B., Yin, X.Q., Zahoor, A. and Wang, H.Y. 2018. Sorption of lead ions onto oxidized bagasse-biochar mitigates Pb-induced oxidative stress on hydroponically grown chicory: Experimental observations and mechanisms. Chemosphere, 208: 887-898.

Shen, Z.T., Hou, D.Y., Jin, F., Shi, J.X., Fan, X.L., Tsang, C.W. and Aless, D.S. 2019. Effect of production temperature on lead removal mechanisms by rice straw biochars. Sci. Total Environ., 655: 751-758.

Shen, Z.T., Jin, F., Wang, F., McMillan, O. and Al-Tabbaa, A. 2015. Sorption of lead by Salisbury biochar produced from British broadleaf hardwood. Bioresource Tech., 193: 553-556.

Shen, Z.T., Zhang, Y.Y., Jin, F., McMillan, O. and Al-Tabbaa, A. 2017. Qualitative and quantitative characterisation of adsorption mechanisms of lead on four biochars. Sci. Total Environ., 609: 1401-1410.

Shi, J.X., Fan, X.L., C.W.T, Wang, D., Shen, F., Hou, Z.T. and Alessi, S.D. 2019. Removal of lead by rice husk biochars produced at different temperatures and implications for their environmental utilizations. Chemosphere, 235: 825-831.

Wan, S.L., Wu, J.Y., Zhou, S.S., Wang, R., Gao, B. and He, F. 2018. Enhanced lead and cadmium removal using biochar-supported hydrated manganese oxide (HMO) nanoparticles: Behavior and mechanism. Sci. Total Environ., 616-617: 1298-1306.

Wang, S., Gao, B., Li, Y., Mosa, A., Zimmerman, A.R., Ma, L.Q., Harris, W.G. and Migliaccio, K.W. 2015. Manganese oxide-modified biochars: Preparation, characterization, and sorption of arsenate and lead. Bioresource Tech., 181: 13-17.

Wang, X.S., Tang, Y.P. and Tao, S.R. 2008. Removal of Cr(VI) from aqueous solutions by the nonliving biomass of Alligator weed: Kinetics and equilibrium. Adsorption J. Int. Adsorption Soc., 14: 823-830.

Xiong, W., Jing, T., Yang, Z., Zeng, G., Zhou, Y., Wang, D., Song, P., Rui, X., Chen, Z. and Min, C. 2017. Adsorption of phosphate from aqueous solution using iron-zirconium modified activated carbon nanofiber: performance and mechanism. J. Colloid Interf. Sci, 493: 17-23.

Yahya, N.Y., Ngadi, N., Jusoh, M. and Halim, N.A.A., 2016. Characterization and parametric study of mesoporous calcium titanate catalyst for transesterification of waste cooking oil into biodiesel. Energy Convers. Manage, 129: 275-283.

Yuan, J.H., Xu, R.K. and Zhang, H. 2011. The forms of alkalis in the biochar produced from crop residues at different temperatures. Bioresource Tech., 102: 3488-3497.

Zhang, J.Q., Hu, X.L., Zhang, K.J. and Xue, Y.W. 2019. Desorption of calcium-rich crayfish shell biochar for the removal of lead from aqueous solutions. J. Colloid Interf. Sci., 554: 417-423.

Zhang, S.Q., Yang, X., Liu, L., Ju, M.T. and Zheng, K. 2018. Adsorption behavior of selective recognition functionalized biochar to Cd(II) in wastewater. Materials, 11: 299-305.

Zhu, X., Liu, Y., Feng, Q., Chao, Z., Zhang, S. and Chen, J. 2014. Preparation of magnetic porous carbon from waste hydrochar by simultaneous activation and magnetization for tetracycline removal. Bioresource Tech., 154(2): 209-214.

Zhou, X.H., Liu, Y.C., Zhou, J.J., Guo, J., Ren, J.L. and Zhou, F. 2018. Efficient removal of lead from aqueous solution by urea-functionalized magnetic biochar: Preparation, characterization and mechanism study. J. Taiwan Inst. Chem. Eng., 91: 457-467.

Zhou, Y.M., Gao, B., Zimmerman, R.A., Fang, J., Sun, Y.N. and Cao, X.D. 2013. Sorption of heavy metals on chitosan-modified biochars and its biological effects. Chem. Eng. J., 231: 512-518.

Zhou, Y.Y., Liu, X.C., Xiang, Y.J., Wang, P., Zhang, J.C., Zhang, F.F., Wei, J.H., Luo, L., Lei, M. and Tang, L. 2017. Modification of biochar derived from sawdust and its application in removal of tetracycline and copper from aqueous solution: Adsorption mechanism and modeling. Bioresource Tech., 245: 266-273.