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Characterization of the Biochar Derived from Peanut Shell and Adsorption of Pb(II) from Aqueous Solutions

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ABSTRACT

With the rapid development of industrial activities, a large amount of industrial effluents containing heavy metals is released into the surface and underground waters. It is highly significant and urgent to develop efficient and cost-effective methods to remove heavy metals from contaminated water. Biochar has been widely used as an adsorbent for the removal of environmental pollutants. In this work, the biochar was derived from peanut shell. The research on the removal of Pb(II) ions in aqueous solution by the biochar was carried out. It can be concluded that the operational parameters, such as pH, contact time and initial concentration of the Pb(II) ions in aqueous solution, had an important effect on the removal of Pb(II) ions. The Langmuir and the Freundlich models were utilized to explain the experimental data. According to results, the adsorption process fitted to the Langmuir model. It was also suggested that the adsorption process was homogeneous adsorption. The Pb(II) in aqueous solution adsorption on the biochar was monolayer adsorption.

INTRODUCTION

With the rapid development of industrial activities, a large amount of industrial effluents containing heavy metals are released into the surface and underground waters. These industrial effluents have resulted in a number of environmental problems (Barakat 2011). Heavy metals, such as lead, copper and cadmium are toxic and non-biodegradable, they can accumulate in living organisms, and may thus pose a threat to human health (Kumar et al. 2014). Therefore, it is very important to develop effective technologies to treat heavy metal polluted wastewaters before their discharge into the natural environment (Wang et al. 2015a).

Lead is especially known to be one of the most toxic metals among heavy metals, even at low concentrations in aquatic environments (Seyda et al. 2014). Current USEPA drinking water standard for lead is 300 μg/L. When present above 0.05 mg/L in drinking water, Pb(II) is a potent neurotoxic metal (Sag et al. 1965). Acute lead poisoning in humans affect the central nervous system, the gastrointestinal system, the liver and kidneys, and it can directly or indirectly cause serious health issues, such as anaemia, hepatitis, nephritic syndrome and encephalopathy (Järup 2003, Momcilovic et al. 2011).

It is highly significant and urgent to develop efficient and cost-effective methods to remove heavy metals from contaminated water. Heretofore, a few classical treatment technologies have been constantly applied and optimized for heavy metal removal from water, including chemical precipitation (Janyasuthiwong et al. 2015, Matthew et al. 2002), adsorption, electro coagulation (Al-Shannag et al. 2015, Elabbas et al. 2016), and membrane filtration (Wang et al. 2013, Mehdipour et al. 2015). Among these technologies, adsorption has been generally regarded as a facile, effective technique for low level heavy metal sequestration, especially for tertiary treatment. From a generic viewpoint, the design of an adsorbent with specific binding sites for heavy metal capture has significant importance. Biochar has been widely used as an adsorbent for the removal of environmental pollutants (Tan et al. 2015). Its feedstocks derived from biomass materials including food waste, sewage sludge, peanut shell, corn stalk, sawdust and other agricultural wastes, which are considered worthless waste. Particularly, modified biochars have a large surface area, fine porous structure and abundant functional groups, which were widely reported as the effective environmental remediation agent for contaminants in polluted soil or wastewater (Zhou et al. 2014).

In this study, the biochar derived from peanut shell was used as a biosorbent for the removal of Pb(II) ions in aqueous solution. In order to enhance the peanut shell, it was treated by K_2CO_3 solution. The operational parameters such as pH, contact time and initial concentration of the Pb(II) ions in aqueous solution, were investigated. The experimental data were discussed using Langmuir and Freundlich models.

MATERIALS AND METHODS

Materials: The peanut shell was obtained from a local farm in Zhejiang province. The peanut shell was first dried for 24h at 383 K in a heating oven. Then, the dried peanut shell was milled to obtain a powder between 1 mm and 2 mm prior to use. A 40 g of peanut shell was immersed in 100 mL of 2% K_2CO_3 solution for 12 h. The mixture was dried at 353 K for 24h. Then, the mixture was put into the muffle furnace at 873 K for 3 h. It was added then into a 250 mL flask containing 7 mL of distilled water. The flask was put into the thermostat water bath and agitated for 2h at 353 K. It was dried for 9h at 383 K in the heating oven and then washed by the distilled water into pH value ranging from 7 to 9. It was dried for 5h at 383 K in the heating oven again and then ground and sifted into 100 meshes for adsorption experiment.

All the chemicals and reagents used in this work were of analytical grade and solutions were prepared using deionized water. The wastewater of Pb^{2+} ion was prepared with the $Pb(NO_3)_2$.

Experimental methods: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing the biochar and 100 mL of Pb^{2+} ion solutions with various initial concentrations. The initial pH was adjusted with 1 mol/L HCl or 1 mol/L NaOH. The flasks were placed in a shaker at a constant temperature and 200 rpm. The samples were filtered and analysed.

Analytical methods: The textural characteristics of the biochar including surface area, pore volume and pore size distribution were determined by standard N_2-adsorption technique. Surface morphology of the samples was determined by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray fluorescence spectroscopy (EDS, Oxford Instruments Link ISIS) for analysing surface elements. The biochar was also characterized by FTIR spectroscopy to identify the type of chemical bonds present in the molecules. The concentration of Pb^{2+} ion was analysed by atomic absorption spectrophotometry (AAS).

The amount of adsorbed Pb^{2+} ion q_t (mg/g) at different times, was calculated as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad ...(1)$$

Where, C_0 and C_t (mg/L) are the initial and equilibrium liquid-phase concentrations of Pb^{2+} ion respectively. V (L) is the solution volume and m(g) is the mass of adsorbent used.

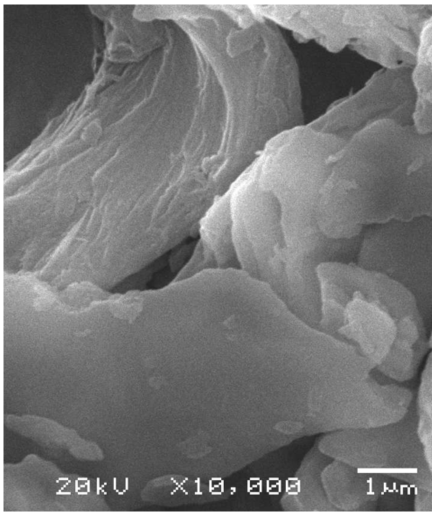

Fig.1: SEM image of the biochar.

Statistical analyses of data: All the experiments were repeated in duplicate and the data of results were the mean and the standard deviation (SD). The value of the SD was calculated by Excel software. All error estimates given in the text and error bars in figures are the standard deviation of means (mean±SD). All statistical significances were noted at α=0.05 unless otherwise stated.

RESULTS AND DISCUSSION

Characterization of the biochar: The SEM images of the surface morphologies of the biochar are shown in Fig. 1. They all have a fully developed and smooth structure in micron-size. As from Fig. 2, the SEM-EDS analysis confirmed the occurrence of K element on the surface of the biochar. The C, O, Al and Si contents of the biochar were 65.49%, 34.05%, 0.13% and 0.15%, respectively.

The biochar also exhibited a high BET specific surface area, total pore volume and micropore volume values. The values are 2.79 m^2/g, 0.003 cm^3/g and 0.0035 cm^3/g respectively.

The structures of the biochar were analysed with FTIR. Fig. 3 shows the FTIR spectra of the biochar in the near IR region (wave number: 4000-400 cm^{-1}).

As shown from Fig. 3, the spectra of the biochar include a band at 3900 cm^{-1} to 4000 cm^{-1}, which is mostly related to the presence of a -O-H- functional group on the surface. The broad band centered at approximately 3900 cm^{-1}. It is attributed to the -O-H- stretching vibration which indicates significant hydrogen-bonding interactions. The peak at

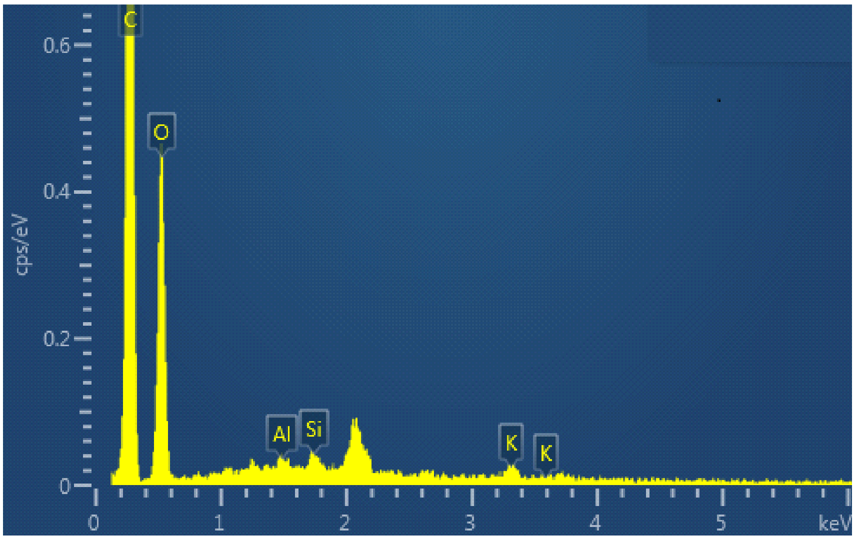

Fig. 2: EDS image of the biochar.

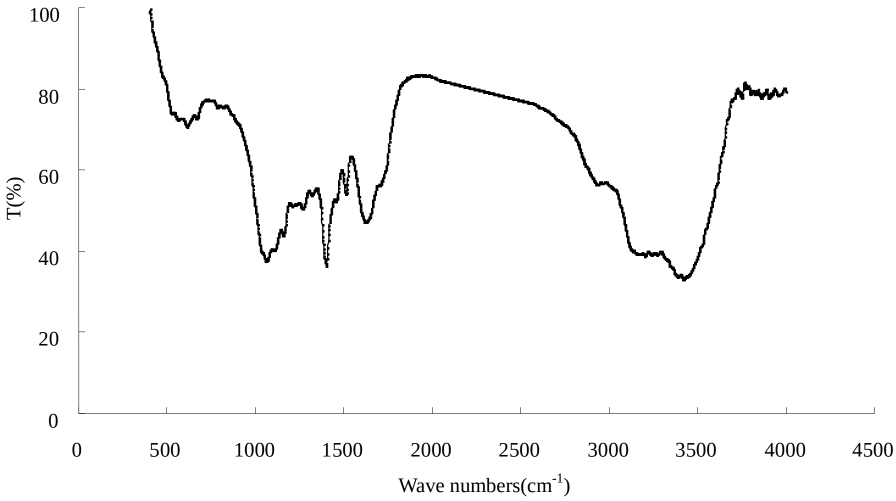

Fig. 3: FTIR spectra of the biochar.

3122 cm^{-1} is attributed to -C=C-H stretching of the functional groups. The peak at 1620 cm^{-1} can be assigned to the -C=C- stretching of benzene ring group. The bands at 1500 and 1060 cm^{-1} may indicate the presence of the inorganic compounds, such as carbonates and silica compounds. When the wave number is under 612 cm^{-1}, it is thought to be the fingerprint region which is related to phosphate and sulphur functional groups.

Effect of pH: It is well known that the pH of the solution is one of the most important parameters in the removal of heavy metals from aqueous solutions. In this study, the effect of pH on the biosorption of Pb(II) ions on the biochar derived from the peanut shell was investigated. These experiments were carried out by changing the initial pH of the solution from 2.0 to 6.0. The pH dependent experiments were not conducted at a pH value higher than 6.0 to avoid the precipitation of Pb(II) ions as hydroxide. The contact time is 240 minutes. The dosage of the biochar is 0.4 g. The concentration of Pb(II) ions in solution is 200 mg/L. The effect of pH in solution on the removal of Pb(II) ions by the biochar is shown in Fig. 4.

Removal of Pb(II) ions (%): From Fig. 4, it can be concluded that the pH had an important role on the removal of Pb(II) ions by the biochar. The removal of Pb(II) ions was increased with the increasing the pH. The increase in pH would promote the removal the heavy metals. Some studies

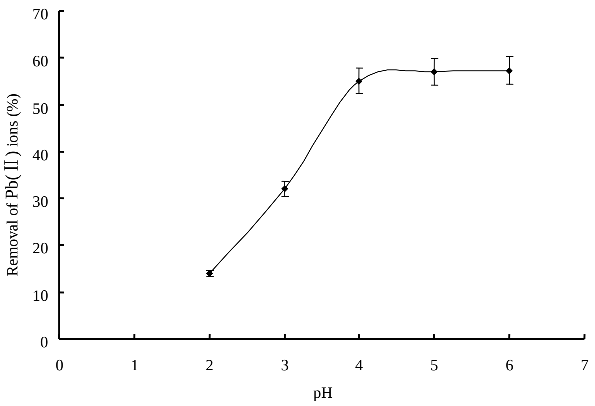

Fig. 4: Effect of pH on the removal of lead ions by the biochar.

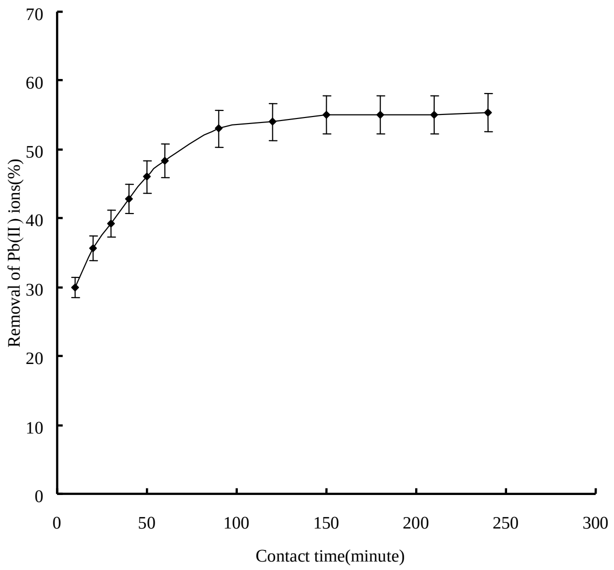

Fig. 5: Effect of contact time on the removal of lead ions by the biochar.

have shown that pH-dependent surface charges play an important role in controlling the surface adsorption of heavy metal ions through electrostatic interactions (Wang et al. 2015b). The removal of Pb(II) ions by the biochar is very low at the pH 2.0. It may be explained on the basis of electrostatic repulsion forces between positively charged H_3O^+ and Pb^{2+} ions (Ozer 2007). There are no significant differences in the removal of Pb(II) ions at the pH values between 4.0 and 6.0. When the pH value increased, the covered H_3O^+ left the biochar surface and made the sites available to Pb(II).

Effect of contact time: The contact time is one of the important parameters in the process of adsorption. The dosage of the biochar is 0.4 g and the concentration of Pb(II) ions in solution is 200 mg/L. The value of pH was adjusted to 4.0. The relationship of removal of the Pb(II) ions with contact time is shown in Fig. 5.

From Fig. 5, it can be shown that the biosorption is relatively rapid in the initial 60 minutes, because the biosorption sites were vacant, and Pb(II) could easily interact with these sites. In addition, the biosorption efficiency increased with contact time. After 120 minutes, the biosorption efficiency was almost constant such that it could be considered the equilibrium time of the Pb(II) biosorption.

Effect of the initial concentration of the Pb(II) ions in aqueous solution: The initial concentration of the Pb(II) ions in aqueous solution had an important role on the removal of Pb(II) ions in aqueous solution by the biochar. The experiments were investigated at pH4.0, contact time of 180 minutes and the dosage of biochar of 0.4 g. The initial concentration of Pb(II) ions in aqueous solution was ranged from 100 mg/L to 400 mg/L. The experimental results are shown in Fig. 6.

Removal of Pb(II) ions (%): The removal of Pb(II) ions in aqueous solution is decreasing with the increasing initial concentration of Pb(II) ions. This result caused lower biosorption yields at the higher concentrations due to the saturation of the biosorption sites. This increase could be due to the increase in electrostatic interactions (related to covalent interactions), involving sites of progressively lower affinity for Pb(II) ions in aqueous solution. Therefore, more Pb(II) ions in aqueous solution were left un-biosorbed in solution at higher concentration levels. These results were in agreement with the results of previous studies (Dhankhar et al. 2011, Karthika et al. 2010).

The adsorption isotherm of Pb(II) ions in aqueous solution by the biochar: It is known that the equilibrium biosorption isotherm is fundamentally important in the design of a biosorption system, because equilibrium studies of biosorption are used to determine the capacity of the biosorbent. The biosorption equilibrium is established, when the concentration of sorbate in bulk solution is in dynamic balance with that on the liquid-sorbent interface. The relationship between the initial concentration and the amount of sorbent is known as the degree of the sorbent affinity for the sorbate which determines its distribution between the solid and liquid phases. Several models are often employed to interpret the equilibrium data. In the present research, the Langmuir and the Freundlich models were utilized to explain the experimental data. The Langmuir model and Freundlich model of linear forms are as below (Liu and Zhang 2011):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad ...(2)$$

Table 1: The adsorption parameters for Pb^{2+} ions adsorption from aqueous solution on the biochar by Langmuir adsorption isotherm and Freundlich isotherm.

Langmuir parameters			Freundlich parameters		
q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F	R^2
111.11	0.11	0.9951	909.09	82.24	0.3998

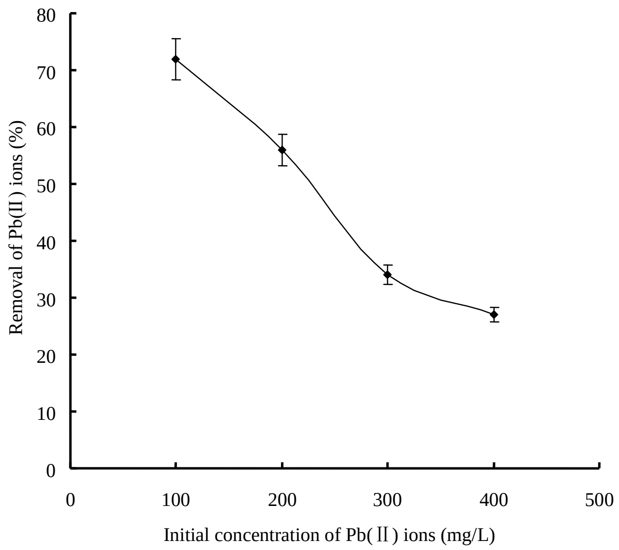

Fig. 6: Effect of initial concentration of the Pb(II) ions in aqueous solution on the removal of lead ions by the biochar.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad ...(3)$$

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.

According to the experimental data, the adsorption parameters were obtained from the Langmuir adsorption isotherm and Freundlich adsorption isotherm (Table 1).

It showed that the Langmuir adsorption isotherm model is more suitable for the Pb^{2+} ion from aqueous solution than the Freundlich adsorption isotherm model. It is also suggested that the adsorption process is homogeneous adsorption. The Pb^{2+} ion from aqueous solution adsorption on the biochar is monolayer adsorption.

CONCLUSIONS

In this study, the research on the removal of Pb(II) ions in aqueous solution by the biochar derived from peanut shell was carried out. The biochar has a fully developed and smooth structure in micron-size. According to the experimental results, the biochar showed much better adsorption ability to Pb(II) ions in aqueous solution. The adsorption of Pb(II) in aqueous solution on the biochar was monolayer adsorption. The biochar derived from peanut shell can be used to remove Pb(II) ions in aqueous solution efficiently.

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