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Rapid and efficient removal of Pb(II) from aqueous solutions using biomass-derived activated carbon with humic acid in-situ modification

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ABSTRACT

This study developed an humic acid (HA) in-situ modified activated carbon adsorbent (AC-HA) for the rapid and efficient removal of Pb(II) from aqueous media, and adsorption mechanisms are discussed. The physicochemical characteristics of activated carbons (AC) were investigated via N_2 adsorption/desorption, scanning electron microscopy (SEM), Boehm's titration method and Fourier transform infrared spectroscopy (FTIR). AC-HA exhibited richer oxygen-containing functional groups than the original AC. In addition, the removal performance of AC-HA (250.0 mg/g) toward Pb(II) was greatly improved compared with the original AC (166.7 mg/g). The batch adsorption study results revealed that the Pb(II) adsorption data were best fit by the pseudo-second-order model of kinetics and Langmuir isotherm of isothermals, and therefore, the effect of the solution pH was studied. The superior performance of AC-HA was attributed to the HA modification, which contains numbers of groups and has a strong π-π interaction binding energy with AC and Pb(II) species. The adsorption mechanisms were confirmed via the XPS study. More importantly, the modified method is simple and has a low cost of production.

1. Introduction

The rapid development of industry is leading to significant heavy metals pollution in developing countries (Chi et al., 2017; Soylak et al., 1996). Heavy metal lead (Pb) is stored in the formations (Lu et al., 2009). Metal Pb in the human body will be oxidized into divalent lead ions, Pb(II). It will replace the body's calcium and zinc ions, thereby, causing significant harm to human body (Pan et al., 2010; Wu et al., 2014). Among many methods for dealing with Pb(II) contamination in water, adsorption by activated carbon (AC) is a rapid and convenient method and has been proven by previous studies (Kadirvelu et al., 2000; Gundogdu et al., 2012; Liu et al., 2013; Qiu et al., 2016; Sreejalekshmi et al., 2009; Yu et al., 2015).

For improving the Pb(II) removal performance by AC from aqueous solutions, chemical treatment methods were used for AC modification such as metallic oxide loading (Reed et al., 2000), surface sulfuration (Macıas-Garcıa et al., 2004), and surface oxidation (Mesquita et al., 2006). In this work, humic acid (HA) was used as a modifying agent for in-situ modification of AC to enhance the Pb(II) removal performance from wastewaters. The reasons for using HA are as follows: (1) many groups, such as carboxylic, phenol, hydroxyl, amine and quinone groups, are included in the HA result in a number of different potential sites for metal ions binding, thereby effectively improving the removal capacity of Pb(II); (2) the enhanced stability and transport, through strong π-π interactions, of HA binds ACs (Yang et al., 2011). The metal ions will be adsorbed by HA, which also forms strong complexes on the AC surfaces. The information on the Pb(II) removal on ACs modified with HA is, therefore, crucial for understanding the modification of ACs and for the removal of heavy metal pollutants. However, the HA in-situ modified AC for Pb(II) removal has not been fully investigated.

Phragmites australis (PA) is widely cultivated due to the extensive construction of constructed wetlands in China (Wu et al., 2011). PA withers in the winter and causes problems for the constructed wetland operation such as poor water quality, matrix obstruction and destruction of landscape. A reasonable harvest of withered PA can be effective to solve these problems (Wang et al., 2015a). The abundant biomass waste of withered PA as a precursor for producing activated carbon is a promising strategy (Gundogdu et al., 2013; Guo et al., 2016a; Guo et al., 2017). This approach results in a high-value use of waste, and the prepared AC contains excellent physical and chemical properties.

The objectives of this work were (1) to study the physicochemical characteristics of the HA-modified AC and compare their removal performance of Pb(II) with the original AC; (2) to investigate the adsorption mechanisms of Pb(II) using the HA-modified ACs according to

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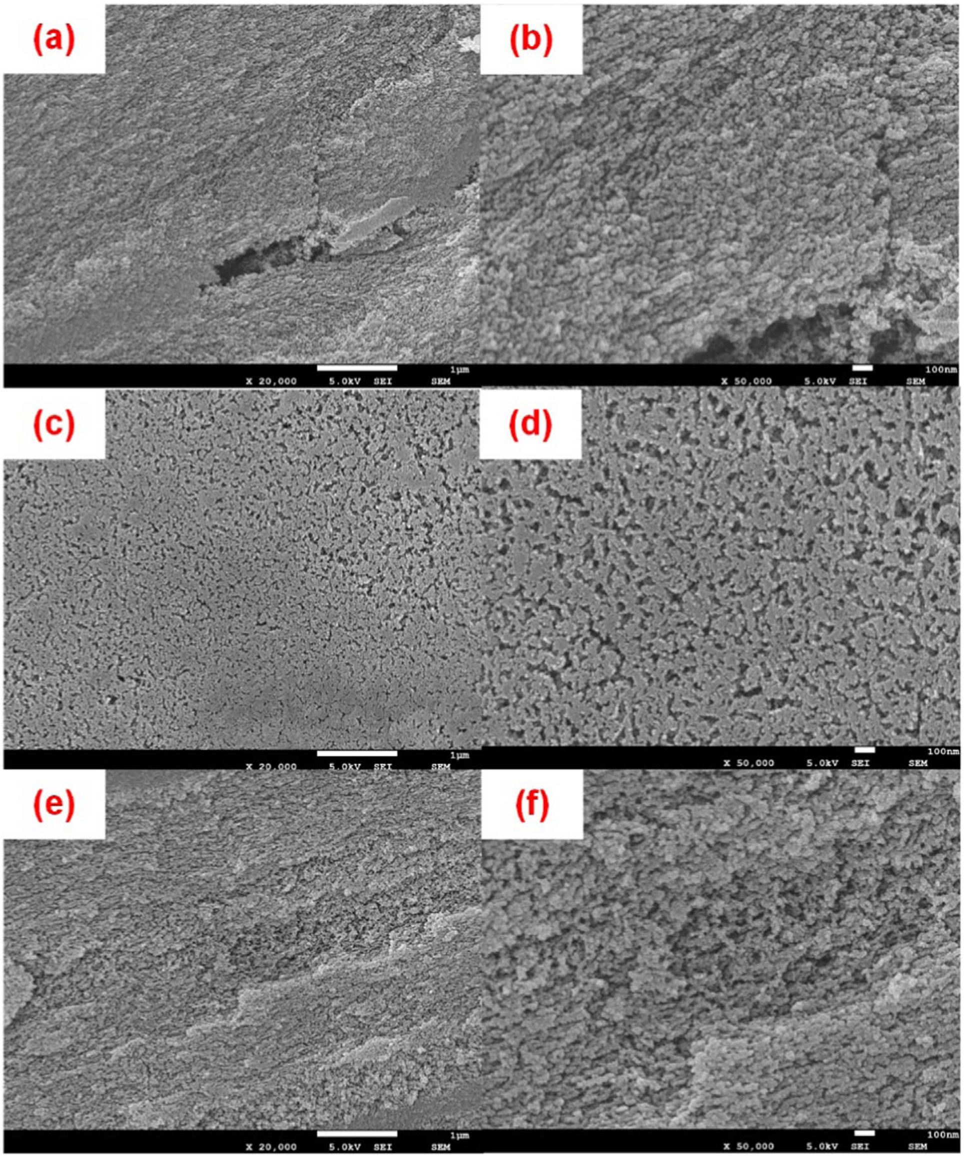

Fig. 1. SEM images of AC (a and b), AC-HA-1 (c and d) and AC-HA-2 (e and f) (a, c and e, magnification 20,000×; b, d and f, magnification 50,000×).

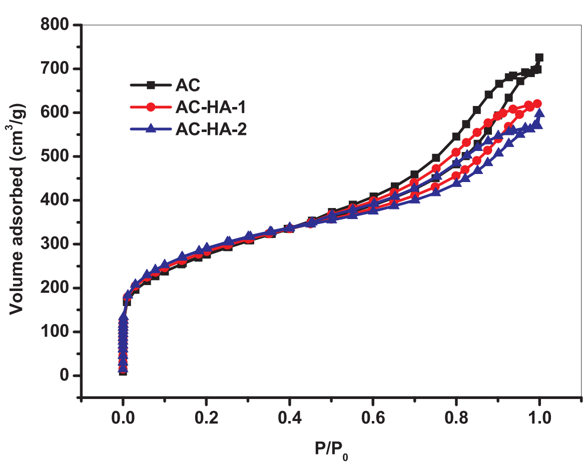

Fig. 2. N_2 adsorption and desorption isotherms of ACs.

Table 1
Textural and chemical characteristics of ACs.

Activated carbons	AC	AC-HA-1	AC-HA-2
S_{BET}[a] (m^2/g)	1057.9	992.3	923.7
S_{mic}[b] (m^2/g)	120.3	178.5	245.9
S_{ext}[c] (m^2 g)	937.6	813.8	677.7
V_{tot}[d] (cm^3/g)	1.12	0.96	0.82
V_{mic}[e] (cm^3/g)	0.06	0.08	0.11
V_{ext}[f] (cm^3/g)	1.06	0.88	0.71
C %	64.77	60.04	57.69
O %	28.01	33.69	36.12
Other %	7.22	6.27	6.19
Carboxylic groups[g] (mmol/g)	0.686	0.943	1.121
Lactonic groups[g] (mmol/g)	0.321	0.439	0.471
Phenolic groups[g] (mmol/g)	0.815	0.961	1.085
Total acidity[g] (mmol/g)	1.822	2.343	2.677

[a] BET surface area (S_{BET}) was determined by using the Brunauer-Emmett-Teller (BET) theory.
[b] Micropore surface area (S_{mic}).
[c] External surface area (S_{ext}).
[d] Total pore volume (V_{tot}) was determined from the amount of N_2 adsorbed at a P/P_0 around 0.95.
[e] Micropore volume (V_{mic}) were evaluated by the *t-plot* method.
[f] External pore volume (V_{ext}).
[g] Results of Boehm's titration of ACs.