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Improving lead adsorption through chemical modification of wheat straw by lactic acid

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Abstract. This work describes the creation of a new cellulosic material derived from wheat straw modified by lactic acid for adsorption of lead in aqueous solution, called 0.3LANS (the concentration of the lactic acid were 0.3mol/L). Batch experiments were conducted to study the effects of initial pH value, contact time, adsorbent dose, initial concentration and temperature. Fourier transform infrared (FTIR), Elemental analysis, BET surface area and Scanning electron micrographs (SEM) analysis were used to investigate the chemical modification. Adsorption isotherm models namely, Langmuir, Freundlich were used to analyse the equilibrium data, and the Langmuir isotherm model provided the best correlation, means that the adsorption was chemical monolayer adsorption and the adsorption capacity q_m was increased with increasing temperature, and reached 51.49mg/g for 0.3LANS at 35℃, showing adsorption was exothermic.

1. Introduction

THE toxic heavy metals found in wastewaters can destroy the ecological balance and affect human body health even at trace concentrations [1]. Heavy metal ions are reported as priority pollutants [2], because of their enrichment and biological toxicity. The toxic effect against living organisms varies owing to the differences between heavy metals, lies on their nature, concentration, mode of action, valence state and bioavailability [3]. Lead is among the most powerful elements damaging the bone hematopoietic system and nervous system by inhibition the function of the enzyme and interfere with the enzyme synthesis. There are many conventional treatment methods, such as chemical precipitation, ion exchange, membrane separation, electrochemistry, adsorption of active carbon, etc. These methods are widely used in the actual operation of the factory; however, their capital costs are much too high to be economical [4]. Some of the methods generate toxic chemical sludge, creating yet another disposal problem subsequently. What's more, there are concentration limits to these methods, they are often ineffective when the concentration of heavy metal ions is lower than 100mg/l. Therefore, looking for new methods is imminent.

Straw as an emerging and promising cellulosic waste materials is characterized by low-cost, effective, renewable and generous, receiving public attention. Many scholars are devoted to the study of straw adsorbent, such as Farajzadeh M. A. [5], Saeed A. [6], and so on. Many researchers turned to the study of modified straw because of the unsatisfactory adsorption effect, for example, the carboxyl

group is introduced by esterification, as Leyva-Ramos R. [1] Torres-Blancas T. [7], Yu Xiaolin [8] et al reported.

The objective of the present study was to use wheat straw (d≤0.2mm) as an adsorbent after modification by lactic acid for the removal of Pb (II) in aqueous model solutions. The effects of the initial lead concentration, pH, contact time, and temperature were studied. What's more, adsorption kinetic and isotherms models were determined in order to study the adsorption mechanism.

2. Materials and methods

2.1. Preparation of the wheat straw
THE wheat straw was washed with running water for several times then dried with natural ventilation, later on, the wheat straw was ground to an average particle size of less than 0.2mm by grinding machine, followed by soak with distilled water for 6h afterwards washed with distilled water and dried at 60℃ in an oven continuously for 24h, until they reached an equilibrium moisture content. Finally, the wheat straw was stored in plastic airtight container, called natural straw(NS).

2.2. Preparation of the modified absorbent
FIRSTLY, NS was processed with 1mol/L NaOH solution by adding 20 g of NS and 200 mL of the NaOH solution in a flask under 200rpm for 2h at indoor temperature (25±0.2℃) to obtain the alkaline NS. After that, The alkaline NS was treated with lactic acid solutions under the same conditions mentioned above. The 0.3LANS was washed several times with distilled water until the pH values no longer changed while washing. At last, they were dried at 60℃ in an oven continuously for 24h, until they reached an equilibrium moisture content, and stored in plastic airtight container for subsequent standby.

2.3. Preparation of the metal solution
THE stock lead solutions (1000mg/L) were prepared by dissolving lead nitrate(PbNO$_3$)in distilled water. The initial pH of the solution was adjusted by using 0.1mol/L HCl or NaOH.

2.4. Experimental design
BATCH adsorption experiments were carried out in 250 mL conical Erlenmeyer flasks containing 150 mL of Pb^{2+} solution with the desired concentration by subjecting a given dose of adsorbent at 150rpm. The mixture was shaking for 2h with a shaker oscillator, time much more than the time it took to achieve adsorption equilibrium. After resting for 5 min, the supernatant was filtered using 0.45 μm microporous filter membrane, and then the concentration of lead ions in the supernatant was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES, optima 7000DV) until the adsorption equilibrium was reached. The percentage removal of Pb^{2+} was calculated using the equation:

$$R = (C_0 - C_e) \times 100\% / C_0 \tag{1}$$

The adsorption capacity q$_e$ (mg/g) was calculated according to the following equation:

$$q_e = (C_0 - C_e)V / m \tag{2}$$

Where C$_o$ and C$_e$ are the initial metal ions concentration and equilibrium metal ions concentration(mg/L), respectively. V is the volume of metal ions solution (L). m is the mass of adsorbent used(g).

3. Results and discussion

3.1. Effect of initial pH

THE pH in the solution will not only affect the concentration of hydrogen ions, but also affect the valence state and morphology of heavy metal ions [9]. The effect of solution pH on the percentage removal of metal ions is shown in Figure 1. The effect of initial pH of the solutions on the removal of Pb^{2+} was studied at different pH ranging from 2.0 to 6.0 because of Pb^{2+} dominates at pH≤6.5, and Pb $(OH)_2$ dominates at pH＞6.5[10]. It was that the adsorption was lower at an initial pH value of 2 on two kinds of adsorbent. A sharp increase occurred in the pH range of 2.0–4.0, at the same time, the removal rate of 0.3LANS was higher than the NS clearly at that range. This variation tendency could be attributed to the fact that Pb (II) is divalent cation, due to the high concentration of active H^+ in the solution at lower pH value, the adsorption capacity is small for which will compete for adsorption sites with heavy metal cations; with the increase of pH value, the gradually reduced concentration of H^+, and the presence of a large number of negatively charged ligands (carboxylic groups) reacting with Pb(II) ions in solution will promote adsorption, and gradually reach the best state, they were 5, 4 of NS and 0.3LANS, respectively. However, with the continuous increase of pH value, the Pb (II) ions in the solution will form hydroxide precipitates, as well as the ionized nature of the cell wall surface of wheat straw [11], which affect the adsorption performance [4].

The effect of pH on removal rate in this study proved the adsorption mechanisms involved both ion exchange and complexation processes, the -COOH group provides acomplexation site, whereas both -OH and -COOH groups generate exchangeable cation sites [12].
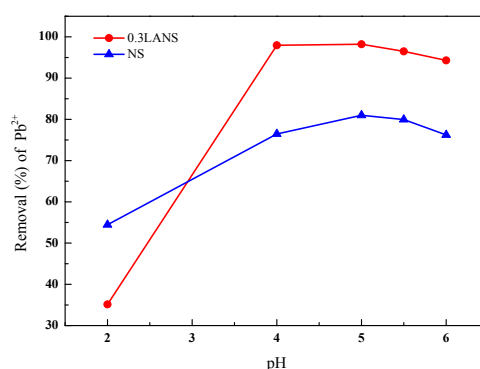

Figure 1. Effects of initial pH for Pb^{2+} by 0.3LANS and NS (m=1g,V=150ml, T=25℃, C_0=100mg/L, d≤0.2mm, shaking speed = 150 rpm, t=2h).

3.2. Effect of the dosage of different adsorbents

THE effect of adsorbent dosage was reflected in the number of adsorption sites. The influence of different adsorbent dosage on the removal of Pb (II) was shown Figure 2. It is obvious that the removal rate increased greatly as the dosage from 0.1g to 1.0g, when more than 1.0g, the removal rate was not increasing, tending to reach the adsorption equilibrium. This could be explained that there were more available adsorption sites as the adsorbent dosage was increased. Under the same adsorption state, the removal rate of 0.3LANS was higher than that of NS, and they are 97%, 79%.
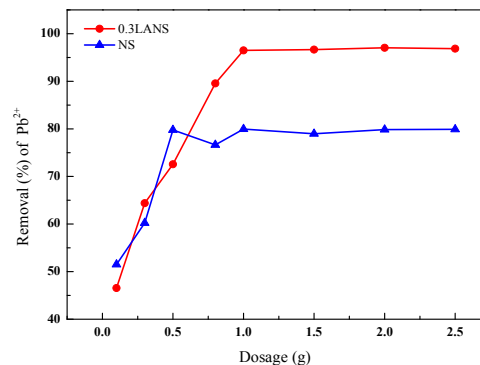
Figure 2. Effect of the adsorbent dosage for Pb^{2+} by 0.3LANS and NS (V=150ml, T=25℃, C_0=100mg/L, d≤0.2mm, shaking speed = 150 rpm, t=2h, pH=5).

3.3. Effect of the contact time and kinetic analysis

THE effect of contact time on adsorption was studied between 0 and 210 min. The adsorption process was very fast. Two kinds of adsorbents could reach the adsorption equilibrium within 60min. After this equilibrium period, there was a very small change in adsorption. Compared with these two adsorbents, the 0.3LANS did not shorten the reaction time, but only showed a strong removal rate under the same experimental conditions. Consequently, 2h of contact time was chosen as the experimental adsorption time for the sake of the balanced achievement.

The experimental data were fitted to the kinetic model called Pseudo-first-order (3) and Pseudo-second-order (4) to make a more intuitive analysis of the kinetic characteristics of the adsorption process. This two models are generally expressed as follow [13]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

Where qt is adsorption capacity at any time t (mg/g), t is contact time(min), k_1 (1/min) is the rate constant of pseudo-first-order adsorption and k_2 (mg/g·min) is the initial adsorption rate of pseudo-second-order adsorption.

The fitting results to two kinds of adsorbents for Pb^{2+} are shown in the Figure 3. and Table 1 compared the fitting results of the two kinetic models. It very clearly that the correlation coefficients of Pseudo-second-order model were higher than 0.99(R^2≥0.99), which means that this model was well to fit the adsorption process in contrast. Thus, the result revealed the whole adsorption process was dominated by chemical reactions, which was consistent with the whole adsorption mechanism.
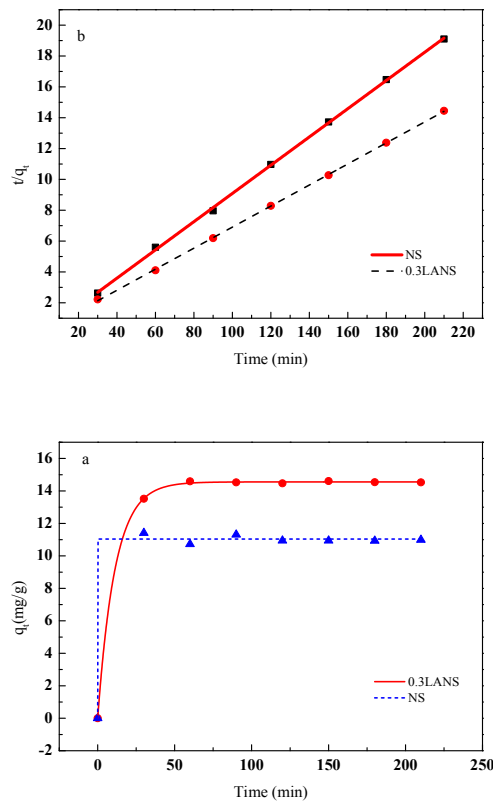
Figure 3. Pseudo-first-order and Pseudo-second-order for Pb^{2+} (a), (b) (m=1g, V=150ml, T=25℃, C_0=100mg/L, d≤0.2mm, shaking speed = 150 rpm, pH=5).

Table 1. Parameter of Pseudo-first-order and Pseudo-second-order for Pb^{2+}

Pb^{2+}	Pseudo-first-order			Pseudo-second-order		
	q_e (mg/ g)	R^2	k_1	q_e(mg/ g)	R^2	k_2
NS	11.034	0.996	2.399	10.922	0.999	-0.128
0.3LANS	14.555	1.000	0.089	14.656	1.000	0.054

3.4. Effect of temperature and adsorption isotherms analysis

NORMALLY, the adsorption isotherms are used to examine the relationship between the concentration remaining in solution of heavy metals and the amount of adsorbent at the interface. The Langmuir and Freundlich models are the most commonly used adsorption models. They can go a step further and optimize the adsorption design, in addition, these provide information about the nature of the material's adsorption and adsorption capacity [14]. The Langmuir model assumes that the solid surface of the adsorbent is uniform and is elucidative for monolayer sorption onto a surface with a finite number of identical sites. It also assumes that the energy relationship represented by the model is that the heat of adsorption does not vary with adsorption, that means all of the adsorption sites on the surface of adsorbent is energetically equivalent [15]. The Freundlich model is an empirical exponential equation based on adsorption on a heterogenous surface [16], which means there is an infinite amount of adsorption on the adsorbent surface. The linear equation of Langmuir and Freundlich models are formulated as follow:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{5}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

Where b (L/g) is the Langmuir constant which is related to the energy of adsorption and affinity of the adsorbent. K_F [(mg/g) (L/mg)$^{1/n}$] and n are Freundlich constants characteristic of the system, indicating the adsorption capacity and adsorption intensity, respectively.

Figure 4. showed the experimental equilibrium data as well as he is fitting results of the two isotherm models. Table 2 showed various parameters calculated from the adsorption isotherms. We can see it that he adsorption process of lead on two modified adsorbents can be better fitted to Langmuir model compared to Freundlich equation, means the surface was completely homogeneous and it was mainly chemical monolayer adsorption [17]. The values of r^2 and b are regarded as a measure of the degree of fitting of experimental data on the isotherm models and the affinity of adsorbent for the metal. For both of them, the greater the value, the better fitting results and the better affinity [18]. Based on the Langmuir equation, the value of q_m increased with increasing temperature, and reached 51.49mg/g for 0.3LANS at 35℃, which confirms that the adsorption process for Pb onto 0.3LANS were endothermic reaction.
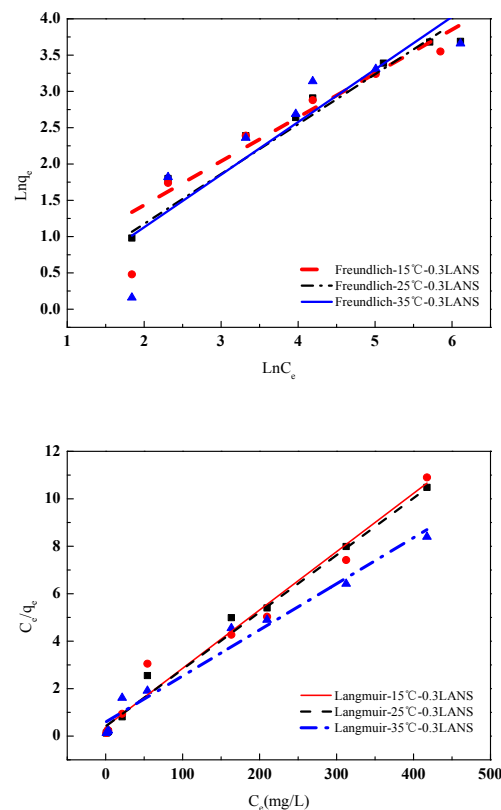

Figure 4. The linearized Langmuir and Freundlich adsorption isotherm of 0.3LANS

3.5. FTIR spectral analysis

FTIR was used to analyse the changes in functional groups before and after modification, thus, it can determine which functional groups were responsible for metal removal. FTIR spectra of NS and 0.3LANS are shown in Figure 5.

The band at 2918 cm^{-1} was attributed to symmetric or asymmetric C-H stretching vibration of lactic acid. The absorption peaks at 1633 and 1426cm^{-1} was assigned to the resulting carboxyl linkage and COO$^-$ symmetric stretching vibration derived from lactic acid [19]. The peaks at 1383 cm^{-1} may be assigned to symmetric stretching of -COO$^-$ of pectin [20]. Bands in the range of 3418 cm^{-1} was indicative of the stretching of O-H group due to inter- and intra-molecular hydrogen bonding of macromolecular association (cellulose, pectin, etc) [21]. The -OH stretching vibrations occur within a broad range of frequencies indicating the presence of "free" hydroxyl groups and bonded -OH bands of carboxylic acids [22]. The peak at 1062cm^{-1} may be assigned to symmetric stretching of C-O stretching vibration. It can be observed from FTIR spectral of wheat straw that the structure of NS was basically the same as 0.3LANS, but there was only a slight gap between them, which showed the effect of the modification. The intensity of hydroxyl in the band of 3418 cm^{-1} was dramatically strengthened and its shape was widened, the same changes took place at band of 1633 and 1383cm^{-1} which means the carboxyl and hydroxyl groups were successfully introduced into wheat straw.

Table 2. Parameter of linearized Langmuir and Freundlich adsorption isotherm for 0.3LANS

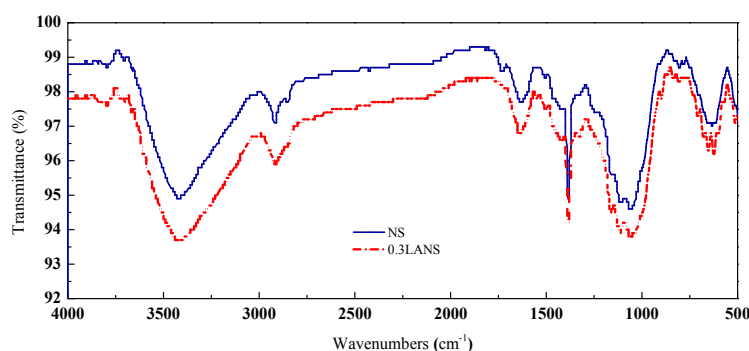| Pb	Langmuir			Freundlich		
	q_m(mg/g)	b(L/mg)	r^2	K_F[mg/(g(mg/L)$^{1/n}$)]	n	r^2
15℃	40.7	0.061	0.987	8.624	3.751	0.939
25℃	41.615	0.058	0.973	8.452	3.555	0.941
35℃	51.493	0.033	0.971	8.797	3.846	0.944

Figure 5. FTIR spectra of NS and 0.3LANS

3.6. Characterization of NS and 0.3LANS

ELEMENTAL analysis results were shown in Table 3. We can conclude that the wheat straw was mainly made up of four elements of C, H, O and N, the content of O elements in 0.3LANS increased compared with NS, because of the introduction of carboxyl groups by chemical reactions, which was consistent with the FTIR analysis results.

BET surface area of NS and 0.3LANS were shown in Table 4. The difference in specific surface area between the two adsorbents was very small, its decrease may be due to new functional groups were introduced to occupy part of the void after modification [23].

Scanning electron micrographs (SEM) analysis were shown in Figure 6. The porosity and inhomogeneity of the original wheat straw were demonstrated by Figure 6A. The structure of NS was loose, and its surface was rough, probably due to the impurity ions on the surface of untreated wheat

straw [24]. The structure of wheat straw modified by lactic acid changed a lot as it showed in Fig.6B. They indicated that particle pores in 0.3LANS were decreased, which are consistent with result of specific surface area, and the surface became more homogeneous and smooth compared to NS. This may be due to the pretreatment of NaOH that removed some impurities (e.g., gums, lipids, etc.).

Table 3. Elemental composition of NS and 0.3LANS

Wheat straw	Weight percentage (%)			
	C	H	O	N
NS	43.83	5.96	45.01	0.24
0.3LANS	42.25	5.88	46.64	0.25

Table 4. BET surface area of NS and 0.3LANS

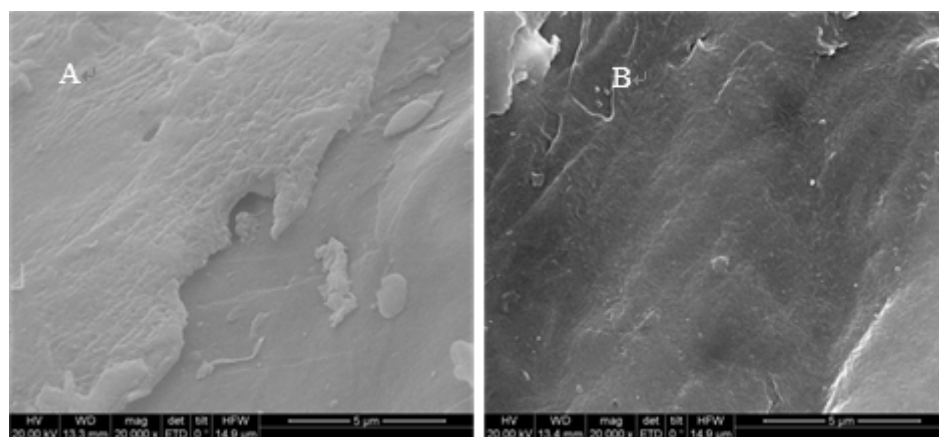|	NS	0.3LANS
BET surface area(m^2/g)	1.4200±0.0218	1.1319±0.0146

Figure 6. Scanning electron microscopy of (A) NS and (B) 0.3LANS

4. Adsorption mechanism

THE adsorption of heavy metal ions is affected by many factors, including types of straw, physical and chemical properties, environmental conditions, etc [25]. However, there are two primary reasons to explain the adsorption process, for one thing, it is the existence of functional groups related to adsorption on the surface of the cell wall, they are hydroxyl, carboxyl, sulfhydryl, amino, and so on, for another it is the surface electrostatic adsorption of straw. The former is chemical adsorption, and it is most critical, the latter is physical adsorption. In the chemical adsorption, ion exchange is the main mechanism, and carboxyl is the main functional group. A study by Marín A.B.P. et al. [26] shows the contribution of carboxyl groups in the sorption of Cd(II), Zn (II) and Cr (III), they focused on the effects of different functional groups (amine, carboxyl and hydroxyl) on the adsorption of heavy metals, and they came to the conclusion that in the adsorption process, pectin and carboxyl play the main role, and the effect of hydroxyl and amino groups was not obvious by chemically modified to prevent the mentioned functional groups. The pH value of the solution decreases with the adsorption process, which is due to the ion exchange between heavy metal ions and H on the adsorbent, many researchers have come to this conclusion, such as Petrović M. et al. [27] and Feng Ningchuan et al. [28]

5. Conclusion

THE adsorption performance of lead were discussed by using wheat straw as raw material in this paper. Metal removal of it can be enhanced by lactic acid treatments. The removal rate of 0.3LANS was higher than that of NS, remarkably, they were 97% and 79%, respectively. The solution pH plays a very important role in the adsorption and it was observed that they were 5, 4 of NS and 0.3LANS, respectively. Both FTIR and elemental analysis confirmed that the carboxyl group was introduced after modification, which was related to the enhancement of adsorption capacity. All in all, straw as adsorbent of heavy metal waste water not only offers a new way for heavy metal wastewater treatment, but also can solve the problem of the disposal of straw, which is a win-win situation.

Acknowledgements

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