



Characterization and lead adsorption properties of activated carbons prepared from cotton stalk by one-step H_3PO_4 activation

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ABSTRACT

Activated carbons were prepared from cotton stalk by one-step H_3PO_4 activation and used as adsorbent for the removal of lead(II). Taguchi experimental design method was used to optimize the preparation of the adsorbents. The results showed that the optimized conditions were: impregnation with a 50% (w/v) phosphoric acid solution with a mass ratio of 3:2 and activation temperature at 500°C for 60 min with the rate of achieving the activation temperature equal to $10^\circ\text{C min}^{-1}$. The cotton stalk activated carbon (CSAC) prepared at these conditions have 1.43 mmol g^{-1} acidic surface groups and $1570 \text{ m}^2 \text{ g}^{-1}$ BET surface area. Adsorption isotherms for lead(II) on the adsorbents were measured by conducting a series of batch adsorption experiments. The Langmuir maximum adsorption amount of lead(II) on CSAC was more than 119 mg g^{-1} , which was superior to the ordinary commercial activated carbon (CAC) on the market. Compared with the CAC, the CSAC had a wider applicable pH range from 3.5 to 6.5 for lead(II) uptake. The final pH values at equilibrium after adsorption were lower than the initial pH value, indicating that the ion-exchange process was involved in the adsorption. This is also confirmed by the result that the increase of acidic surface groups favored the adsorption process. Thermodynamic study indicated that the adsorption was a spontaneous and endothermic process.

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1. Introduction

Lead is an important compound used as an intermediate in processing industries such as plating, paint and dyes, glass operations, and lead batteries [1,2]. The permissible limit of lead in drinking water and surface water intended for drinking, as set by EU, USEPA and WHO, are 0.010, 0.015 and 0.010 mg L^{-1} , respectively [3,4]. The presence of excess lead in drinking water causes diseases such as anemia, encephalopathy, and hepatitis [5].

Various techniques such as chemical precipitation, ion-exchange, membrane filtration, reverse osmosis or adsorption have been developed to remove lead(II) from wastewater [6–8]. Adsorption is considered quite attractive in terms of its efficiency of removal from dilute solutions. Activated carbons (ACs) have been widely used in wastewater treatments to remove inorganic or organic pollutants because of their huge specific surface area, high adsorption capacity and rate, and specific surface reactivity [9,10]. The adsorptive capacity of ACs is not only determined by the adsorbent's textural or porous structure but is also strongly influenced by the chemical structures of the surface [11]. This is because on the adsorbent surface there might be unpaired electrons, incompletely

saturated valences and/or certain functional groups, which would undoubtedly influence the surface attraction force and ultimately the adsorptive capacity, particularly when additional amounts of adsorbate are taken up onto the adsorbent via chemisorption [12]. Moreover, the textural and chemical characteristics of the adsorbent depend on the methods and conditions of production as well as the nature of the precursor used for producing the adsorbent.

The manufacture of ACs can be classified into two methods: physical and chemical processes. Chemical process is now widely applied because of its lower activation temperature and higher product yield compared to physical process. Phosphoric acid is the preferred processing method because of the low activation temperature compared to physical activation [13]. Furthermore, phosphoric acid activated carbons exhibit remarkable cation-exchange capacity, which has proven to be highly effective adsorbents to remove low concentration heavy metal ions from aqueous phase [14,15]; and this capacity is chemically and thermally stable [16]. Therefore, phosphoric acid activated carbons have been widely used to remove heavy metal ions from water phase.

Cotton is the main crop in China, and the planting area is more than 5.5 million ha, and it is estimated that more than 20 million tons (dry weight) of cotton stalk are generated annually [17]. In recent years, it has prompted a growing research interest in the production of activated carbon from renewable and cheaper

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precursors which are mainly renewable biomass materials including grain sorghum [13], coir pith [18], apricot stone [19], pecan shell [14,20], rubber wood sawdust [21], crop-residue [22] and oil palm fibre [23]. So it is proposed to make cotton stalk into activated carbon in order to make better use of these cheap and abundant biomass materials.

In this work, low-cost cotton stalk activated carbons with plenty of surface oxygen-containing functional groups were prepared by one-step H_3PO_4 activation for the removal of lead(II). Taguchi optimization method was used to investigate the effect of the operational parameters such as impregnation ratio, H_3PO_4 concentration, activation temperature, the rate of achieving the activation temperature and activation time on the adsorption ability of the prepared activated carbons. Also, it was used to find the best level of each parameter for lead(II) adsorption in the preparation of AC from cotton stalk. The characteristics, the adsorption ability and thermodynamic of lead(II) onto the CSAC prepared at optimized conditions were investigated for the design of adsorption process, as well.

2. Methods

2.1. Preparation of adsorbents

The precursor used for the production of adsorbent was cotton stalk. The precursor was crushed and sieved through the mesh number 10 (approximately 2 mm), and was soaked with phosphoric acid solution (30, 40, 50, 60%, w/v) at an impregnation rate (weight of phosphoric acid/weight of raw material: 0.5, 1, 1.5, 2) for an over night, then was dried in an oven at 105 °C. After that, the carbonization of the dried stalk was carried out under a high purity nitrogen flow of 80 cm³ min⁻¹ by raising the temperature at a rate (5, 10, 15, 20 °C min⁻¹) until activation temperature (350, 400, 500 or 600 °C), and kept at this temperature for 30, 60, 90 or 120 min. Finally, the produced activated carbons were cooled in the inert atmosphere and washed with HCl 0.1 mol L⁻¹ solution and then with double distilled water until the pH of washing effluent reached 6–7. The cotton stalk activated carbon prepared at optimum conditions is designated as CSAC. Commercial activated carbon (CAC) obtained from Nantong Carbon Co., China was used for comparison studies.

2.2. Adsorbent characterization

All the activated carbons used in this work were washed three times in deionized water and dried at 105 °C for 24 h. Then the adsorbents were screened to obtain a particle size range of 0.03–0.08 cm. The pore structures of ACs were investigated by using a computer controlled automated porosimeter (Micromeritics ASAP-2020, America). The S_{BET} was calculated by the BET equation, and the total pore volume was obtained by converting the nitrogen adsorption amount at a relative pressure of 0.98 to the liquid nitrogen volume. The micropore volume (V_{micro}) was deduced using the Dubinin-Astakhov method. The mesopore volume (V_{BJH}) was deduced using the BJH method.

The elemental analysis of the adsorbents was obtained from a CHN-O-Rapid Elemental Analytical Instrument (Elementer, Germany). The pH at the point of zero charge (pH_{PZC}) was determined by batch equilibrium method described by Babic [24]. The FTIR spectra were recorded using an infrared spectrometer (NEXUS870 America-Nicolet) between wavenumbers of 4000 and 400 cm⁻¹. A scanning electron microscope (Hitachi S4800, Japan) was used to visualize the surface morphology and structure of the activated carbon.

2.3. Chemicals

All chemicals and reagents used were of analytical grade and purchased from Shanghai Chemical Reagent Co., China. Stock solutions of lead(II) were prepared from lead nitrate in deionized water. APHS-2C pH meter (Shanghai Kangyi Instrument Co., China) was used to measure the pH values of the solutions. A constant temperature shaker (Shanghai Scientific Instrument Co. Ltd., China) was used for adsorption experiments. The concentrations of lead(II) were determined by atomic absorption spectrometer (AAS; model SOLAAR M6, Thermo). Solutions of 0.1 mol L⁻¹ NaOH and 0.1 mol L⁻¹ HNO₃ were used for pH adjustment. Constant ionic strength 0.1 mol L⁻¹ NaNO₃ was used in all experiments. All working solutions were prepared by diluting the stock solutions with deionized water.

2.4. Adsorption studies

Batch-mode adsorption studies were carried out by using the necessary adsorbents in a 250 mL stopper conical flask containing 100 mL of test solution at a desired pH value, contact time and adsorbent dosage level. Different initial concentration of lead(II) solutions was prepared by proper dilution from stock 500 mg L⁻¹ lead(II) standard. The pH of the experimental solutions was adjusted by adding 0.1 M HNO₃ and 0.1 M NaOH solution as required. About 0.1000 g dried adsorbent was then added, and contents in the flask were shaken in an electrically thermo stated reciprocating shaker at a constant speed of 150 rpm for 48 h to reach adsorption equilibrium conditions. The contents of the flask were filtered and the concentrations of Pb(II) ions were determined.

The amount of adsorbed lead(II) ions was calculated from the mass balance expression given by

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of lead(II) (mg L⁻¹), respectively, V is the volume of the solution (L), and W is the mass of adsorbent (g).

In order to determine the adsorption isotherms and thermodynamic parameters, adsorption tests were performed by adding 0.1000 g adsorbent into 100 mL solutions of lead(II) with different initial concentration of 30–200 mg L⁻¹ at 15, 25 and 35 °C. The pH of the experimental solutions was adjusted by adding 0.1 M HNO₃ and 0.1 M NaOH solution to remain at 4.3 for CSAC and 5.7 for CAC.

The effect of pH on the adsorption of lead(II) was carried out by equilibrating the adsorption mixture with 0.1000 g dried adsorbent and 100 mL of 100 mg L⁻¹ lead(II) ions solution at different pH from 2.0 to 9.0 at 25 °C. The pH values before and after adsorption were measured. The optimum pH for the adsorption process was confirmed from the above experiment.

All the adsorption tests were carried out in duplicate to confirm reproducibility of the experimental results. The reproducibility and relative standard deviation (R.S.D.) are of the order of ±0.5% and ±3%, respectively.

2.5. Orthogonal array and experimental parameters

Taguchi method provides a systematic and efficient approach for conducting experiment during research and development to determine near-optimum settings of design parameters in view of performance and cost [25]. The Taguchi technique applies fractional factorial experimental designs, called orthogonal arrays, to reduce the number of experiments and meanwhile obtaining statistically meaningful results [26]. The selection of a suitable orthogonal array depends on the number of control factors and their levels. By inspecting practical observation, five selected control factors and

Table 1

Parameters and their values corresponding to their levels to be studied in experiments.

Parameters	Levels			
	1	2	3	4
A. Concentration of activation agent H ₃ PO ₄ (% w/v)	30	40	50	60
B. Impregnation ratio	1:2	1:1	3:2	2:1
C. Rate of achieving the activation temperature (°C min ⁻¹)	2	5	10	15
D. Activation temperature (°C)	350	400	500	600
E. Activation time (min ⁻¹)	30	60	90	120

Table 2

The L16 orthogonal array of designed experiments for the preparation of AC and the lead(II) adsorption capacity for each prepared AC sample and corresponding S/N ratios.

Run	Control parameters and their levels					<i>q_{e,lead}</i> (mg g ⁻¹)		
	A	B	C	D	E	Y1	Y2	S/N
1	1	1	1	1	1	26.21	27.86	28.62
2	1	2	2	2	2	43.23	45.14	32.89
3	1	3	3	3	3	49.32	48.48	33.78
4	1	4	4	4	4	31.21	27.93	29.37
5	2	1	2	3	4	50.52	52.24	34.21
6	2	2	1	4	3	48.03	47.97	33.62
7	2	3	4	1	2	63.59	65.17	36.17
8	2	4	3	2	1	68.59	69.24	36.76
9	3	1	3	4	2	73.86	72.55	37.28
10	3	2	4	3	1	79.66	81.21	38.10
11	3	3	1	2	4	74.83	76.86	37.59
12	3	4	2	1	3	67.66	66.41	36.52
13	4	1	4	2	3	53.07	52.55	34.45
14	4	2	3	1	4	52.41	53.62	34.48
15	4	3	2	4	1	61.69	63.21	35.91
16	4	4	1	3	2	74.10	73.38	37.35

their levels applied in this study are listed in Table 1. These control parameters include activation agent concentration (parameter A), impregnation ratio (weight ratio of H₃PO₄ solution and raw material, parameter B), the rate of achieving the activation temperature (parameter C), activation temperature (parameter D), and activation time (parameter E). All control factors have four levels. With the selection of L16 orthogonal array, using five mentioned parameters and their levels, shown in Table 2. The number in table indicates the levels of a factor [27].

Taguchi method recommends the use of the loss function to measure the performance characteristics deviating from the desired value. The value of the loss function is further transformed into signal-to-noise (S/N) ratio. The optimum conditions should be determined using the S/N ratio of the results obtained from experiments designed by orthogonal array technique. There are three basic S/N ratios, the larger-the-better, the smaller-the-better and the nominal-the-better. The larger S/N ratio corresponds to better performance characteristic. Since the optimized conditions are equal to the higher adsorption ability of the adsorbent, “the bigger-the-better” algorithm for the calculation of S/N ratio was chosen [28]. The S/N ratio is calculated using the following equation:

$$\frac{S}{N} = -10 \log \left[\frac{1}{n} \sum \frac{1}{y_i^2} \right] \quad (2)$$

where y_i is the characteristic property, n is the replication number of the experiment. The unit of S/N ratio is decibel (dB), which is frequently used in communication engineering.

3. Results and discussion

3.1. Optimization of adsorbent preparation conditions

3.1.1. Analysis of variance

The lead(II) adsorption capacity on the prepared activated carbons at 25 °C and their corresponding S/N ratios are shown in Table 2. The results of ANOVA analysis for the S/N ratios are shown in Table 3. The purpose of the ANOVA is to investigate which preparation parameter significantly affects the performance characteristic and the contribution of each parameter on the adsorption efficiency. The percentage contribution of each parameter in the total sum of the squared deviations can be used to evaluate the importance of the parameter change on the performance characteristic [28]. According to the results of ANOVA in Table 3, activation agent concentration, with 71.05% contribution, has the highest effect on lead(II) adsorption ability of the prepared ACs. Activation temperature, impregnation ratio, activation time and the rate of achieving the activation temperature have less influence, respectively.

3.1.2. Level average response analysis

The mean S/N ratio for each level of the parameters was summarized as S/N response, which was shown in Table 3. The analysis is done by averaging the S/N data at each level of each factor. The level average responses from the plots based on the S/N data help in optimizing the objective function under study. The experimental condition having the maximum S/N ratio is considered as the optimal condition as the variability characteristics is inversely proportional to the S/N ratio [29]. Thus the optimum condition for CSAC preparation can be determined as the levels corresponding to the largest average S/N ratio. That is activation agent concentration: 50% (level 3); impregnation ratio: 1.5 (level 3); the rate of achieving the activation temperature (parameter C): 10 °C min⁻¹ (level 3); activation temperature: 500 °C (level 3); and activation time: 60 min (level 2).

3.2. Physical and chemical characterization of the adsorbents

3.2.1. Surface area and pore structure characterization

Table 4 gives the BET surface area (S_{BET}), total pore volume (V_{total}), micropore volume (V_{micro}), mesopore volume (V_{BJH}) and average pore diameter (D_p) of the CSAC prepared at the optimum conditions and the commercial carbon CAC. It is found that the CSAC has a high BET surface area of 1570 m² g⁻¹. The average pore diameter is 2.303 nm, indicative of its mesoporous character defined by IUPAC (International Union of Pure & Applied Chemistry). The commercial activated carbon of CAC has the higher surface area and micropore volume than CSAC. The average pore diameter of CAC is 1.923 nm and percentage of micropore volume is 77.7%, showing that the carbon is dominantly micropores.

3.2.2. Fourier transform infrared spectroscopy

To qualitatively characterize surface groups on the two carbons, FTIR transmission spectra were collected for the two samples in this study (Fig. 1). A broad band located around 3345 cm⁻¹ is attributed to hydroxyl groups or adsorbed water. The band around 1570 cm⁻¹ is usually caused by the stretching vibration of C=O in ketones, aldehydes, lactones, and carboxyl groups [30]; the band around 1152 cm⁻¹ is attributed to aromatic ring or C–O–C stretching vibration in ethers [30,31]. The peak at 521 cm⁻¹ may be assigned to the stretching bands of C–O–C, P=O or C–OH [30,32]. As can be inferred from FTIR analysis, there is presence of surface functional groups containing oxygen like carboxylic, carbonyl, phenolic and lactonic groups on the CSAC surface. The bands are strong with CSAC, but invisible or weak with CAC, suggesting higher contents

Table 3
The ANOVA analysis and average effect response for S/N ratios.

Parameters	Sum of squares	DOF	Variance	F-Ratio	Percent (%)	Level average			
						Level 1	Level 2	Level 3	Level 4
A	82.04	3	27.35	–	71.05	31.18	35.19	37.38	35.55
B	10.05	3	3.35	–	8.71	33.65	34.78	35.87	35.01
C	3.78	3	1.26	–	3.27	34.30	34.89	35.59	34.53
D	11.24	3	3.75	–	9.73	33.95	35.43	35.87	34.05
E	8.35	3	2.78	–	7.23	34.86	35.93	34.60	33.92
Error	0.00	0	0.00						
Total	115.47	15							

DOF, Degree of freedom.

The bold values are the maximum average S/N performances of factors in the four different levels at each factor. The largest S/N performance corresponds to the best performance characteristic.

Table 4
Main characteristics of the two activated carbons.

Parameters	CAC	CSAC		
S_{BET} ($\text{m}^2 \text{g}^{-1}$)	1736	1570		
V_{total} ($\text{cm}^3 \text{g}^{-1}$)	0.835	0.904		
V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	0.649	0.601		
V_{BJH} ($\text{cm}^3 \text{g}^{-1}$)	0.093	0.362		
D_p (nm)	1.923	2.303		
pH_{PZC}	5.7	4.3		
Elemental analysis (wt.%)			C	88.32
			H	0.44
			N	0.51
			O	10.73
Acidic surface functional groups (mmol g^{-1})			Carboxylic	Non
			Phenolic	0.07
			Lactonic	0.09
			Carbonyl	0.12
				81.87
				2.61
				4.46
				11.08

of surface functional groups of the former carbon as compared with the latter.

3.2.3. Elemental analysis

As seen in Table 4, the elemental analysis showed that the CSAC has higher contents of hydrogen and oxygen than CAC, suggesting that the former possesses more surface oxygen-containing functional groups [32]. This is also manifested by the Boehm titration that the CSAC has higher contents of carboxylic, lactonic, and phenolic groups than CAC. The CSAC has 1.43 mmol g^{-1} acidic surface groups, which is more than that on CAC. This is further confirmed by the lower pH_{PZC} value of CSAC than that of CAC.

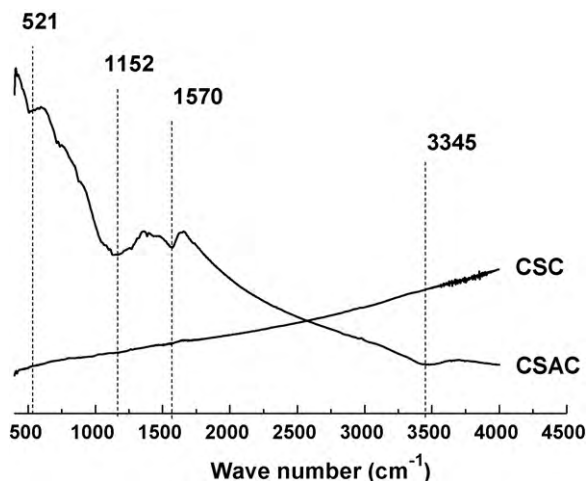


Fig. 1. FTIR spectra of two selected activated carbons.

3.2.4. SEM analysis of the activated carbons

The SEM images of CSAC at different magnifications are shown in Fig. 2. It can be seen from the micrographs that the external surface of the activated carbon is full of cavities, and the pores are different sizes and different shapes. There are much mesopores on the surface on CSAC, which is consistent with the result calculated from N_2 adsorption isotherm at -196°C .

3.3. Lead(II) adsorption capacity

3.3.1. Lead(II) adsorption isotherms

The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. Adsorption isotherms for lead(II) for the CSAC and CAC at 25°C are shown in Fig. 3. It is can be seen that the CSAC prepared in this study had higher lead(II) equilibrium adsorption capacity than the commercial carbon CAC. To understand the adsorption patterns, the Langmuir and Freundlich equations were employed to simulate the adsorption isotherms.

$$q_e = \frac{K_L q^0 C_e}{1 + K_L C_e} \quad (3)$$

$$q_e = K_F C_e^{1/n} \quad (4)$$

where C_e is the equilibrium solution concentration (mg L^{-1}) and q_e is the amount of lead(II) adsorbed onto adsorbents at equilibrium (mg g^{-1}). q^0 and K_L are the Langmuir constants related to the adsorption capacity (mg g^{-1}) and energy of adsorption (L mg^{-1}) respectively. K_F and n are the Freundlich constants related to adsorption capacity and energy of adsorption respectively.

Isotherm parameters of the two models obtained by using non-linear regression are listed in Table 5. The application of the

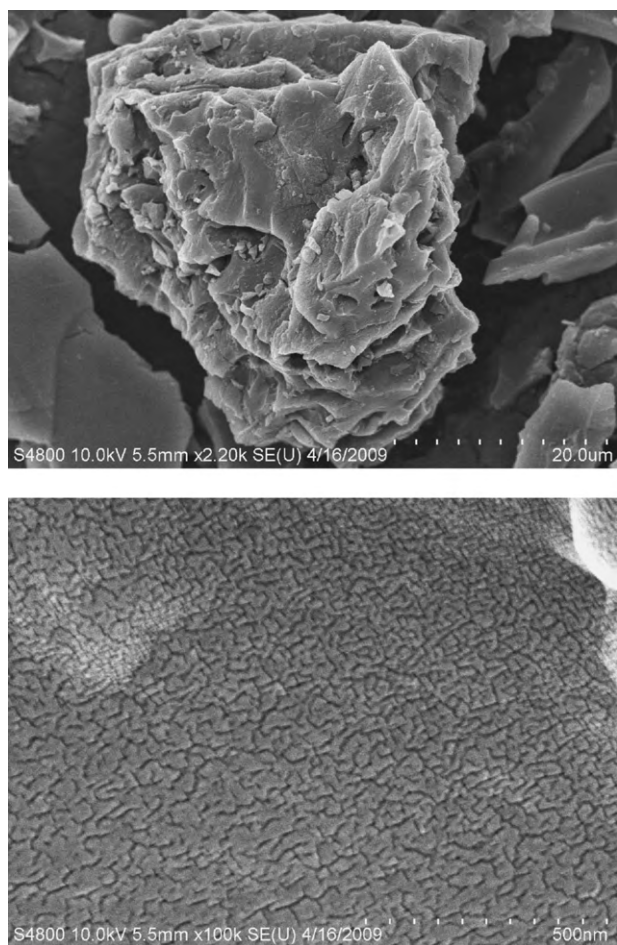


Fig. 2. The SEM images of CSAC at different magnifications.

Langmuir isotherm model is based on the assumption that the binding of adsorbate onto the surface of adsorbent is primarily by a chemical adsorption reaction and all sites possess equal affinity for the adsorbate [33]. The Freundlich isotherm model is an empirical equation based on adsorption onto heterogeneous surfaces [34]. As suggested by the squared correlation coefficient values (R^2) in Table 5, the adsorption data of the adsorbents were well simulated with both the Langmuir and Freundlich models. In order to fur-

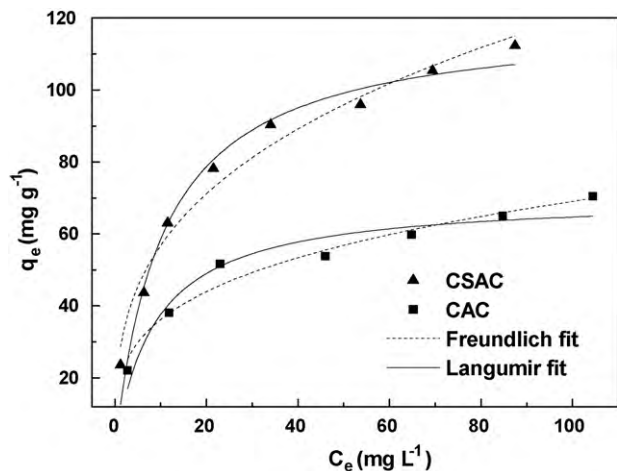


Fig. 3. Comparison of adsorption isotherms for lead(II) on the two different activated carbons at 25 °C.

Table 5

Isotherm parameters for lead(II) adsorption onto the two carbons.

Isotherms	Parameters	CAC	CSAC
Langmuir	q^0 (mg g^{-1})	70.32	119.95
	b (L mg^{-1})	0.115	0.095
	R^2	0.929	0.963
	Δq (%)	7.34	7.78
Freundlich	K_F (L mg^{-1})	18.98	26.83
	n	3.567	3.071
	R^2	0.965	0.975
	Δq (%)	2.54	2.17

ther compare the validity of each isotherm model, a normalized standard deviation $\Delta q(\%)$ was calculated using the Eq. (5).

$$\Delta q(\%) = 100 \sqrt{\frac{\sum [(q_{\text{exp}} - q_{\text{cal}})/q_{\text{exp}}]^2}{N - 1}} \quad (5)$$

where q_{exp} and q_{cal} are experimental and calculated amount of lead(II) adsorbed on the adsorbents, and N is the number of measurements made. It can be found that the values of $\Delta q(\%)$ for the Freundlich equation are all lower than those for the Langmuir equation. This result indicated that the empirical Freundlich equation is better than the Langmuir equation in describing the behavior of lead(II) adsorption onto the two adsorbents, implying that the adsorption process involved multimolecular layers of coverage [35].

From Table 5, it is also observed that the values of n are all larger than 3, indicating that the lead(II) adsorption on the two carbons was favorable [34,36]. Maximum adsorption amount [q^0 (mg g^{-1})] of lead(II) was found to be 119 for CSAC, which was about 1.7 times of that of the CAC (70 mg g^{-1}). The heat of adsorption, as indicated by the K_F values, of the CSAC was also much higher than that of the CAC. The above results suggested that the prepared CSAC is an effective adsorbent for the purification of wastewater polluted with lead(II).

The higher adsorption capacity of lead(II) on CSAC than CAC may relate to the physical and chemical characterization of the adsorbents. It is known that lead(II) adsorption onto activated carbon is influenced by both the textural characteristics and surface chemistry of the carbons [11]. Increasing the BET surface area, micropore volume and surface oxygen-containing groups of the carbons promotes the adsorption of lead ions [37]. The CSAC has a higher adsorption capacity than CAC, which should be due to the higher contents of carboxyl, lactonic, and phenolic groups on the former carbon than CAC since there are lower surface area and micropore volume on the former carbons [15,37].

3.3.2. Effect of pH on the adsorption

The pH of solution has been identified as the most important variable governing metal adsorption on the adsorbent [38]. The effect of pH on lead(II) adsorption onto the two carbons was studied over a pH range of 2.0–9.0 at 25 °C. The procedure outlined in the experimental section was followed with 0.1 g of adsorbent and 100 mL of 100 mg L^{-1} lead(II) solution at a desired pH. As shown in Fig. 4, it is apparent that the equilibrium adsorption amount of lead(II) on the two adsorbents increased greatly with increasing pH, and then decreased slightly with a further increase of pH. As the pH was increased in low pH range, the uptake of lead(II) by the two adsorbents increased. The maximum adsorption was reached at an equilibrium pH of 4.4 for CSAC and 5.8 for CAC, respectively. As the pH was further increased, the adsorption slightly decreased. For the CSAC, there was a wide applicable pH range from 3.5 to 6.5. However, the applicable pH range of the CAC was rather narrow of only 5.5–6.5.

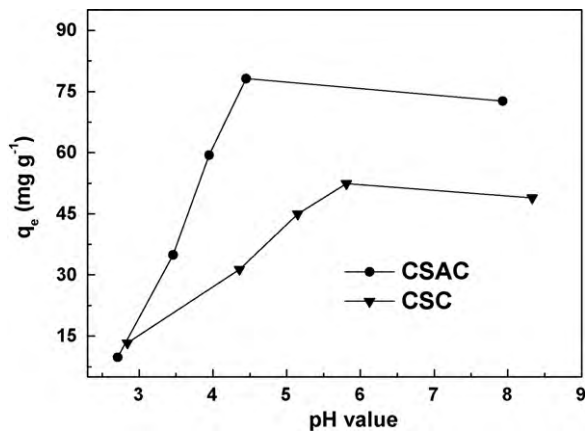
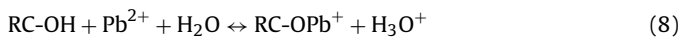


Fig. 4. The effect of solution pH on the adsorption of lead(II) onto the two adsorbents.

The main factors influencing the pH on adsorption process are pH_{pzc} and speciation of lead in aqueous phase. Most lead species exist as lead(II) ions in acidic medium particularly with pH below 6.0, and only a very small portion of $Pb(OH)^+$ ions are present in case of pH approaching 6.0 [39]. The pH_{pzc} of CSAC and CAC are 4.3 and 5.7, respectively. It is found that below pH_{pzc} the surface carries positive charge and vice versa. As the pH decreases in low pH range, the positively charged lead species may be repelled by the positively charged carbon surface molecules which results in a decrease in the percentage adsorption. The decrease of the adsorption at higher pH around 6–9 could be attributed to the formation of lead hydroxide [40].

Table 6 shows the pH values before and after lead(II) adsorption on the two selected carbons. It can be seen that final pH values at adsorption equilibrium are always lower than the initial pH values. It is deduced that H^+ ions were released into the solution as lead(II) got adsorbed on the surface of adsorbent. This lead to the conclusion that the CSAC acted as anion exchangers, which was responsible for the higher adsorption capacity for the CSAC than CAC since the former has a higher content of carboxyl, lactonic, and phenolic groups than the later. An inner sphere complex formation mechanism by ligand exchange process can be predicted for the adsorption process. The surface H^+ groups of carbons would be exchanged with lead in the aqueous phase as follows [41,42]:



3.3.3. Effect of temperature on the adsorption

Graphic presentations of lead(II) adsorption on the CSAC at the experimental temperature of 15, 25, and 35 °C are shown in Fig. 5. It was found that the equilibrium adsorption amount q_e increased with increasing temperature, indicating that the adsorption was an endothermic process. As we know, the physical adsorption is generally exothermic reaction. Hence, logical cause of the observation is that the adsorption should include some endothermic chemical reactions. This is also supported by the positive values of enthalpy change (ΔH^0).

Table 6

The solution pH values before and after lead(II) adsorption onto the carbons.

pH ₀	Adsorbent	2.52	4.04	5.11	6.01	8.81
PH _F	CSAC	2.71	3.46	3.95	4.45	7.93
	CAC	2.84	4.36	5.15	5.81	8.33

pH₀, initial pH value before adsorption; PH_F, equilibrium solution pH after adsorption.

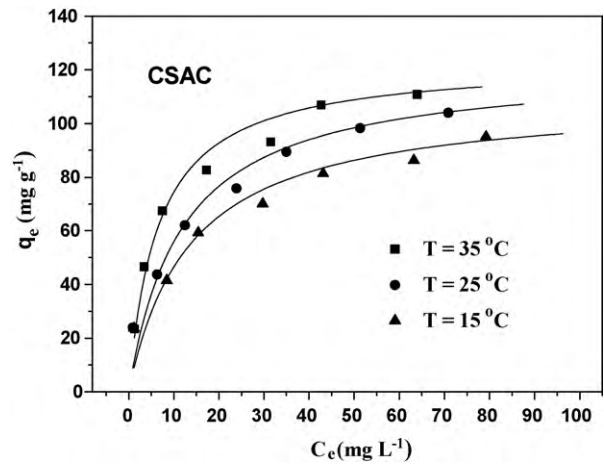


Fig. 5. Adsorption isotherms for lead(II) onto the CSAC at different temperatures.

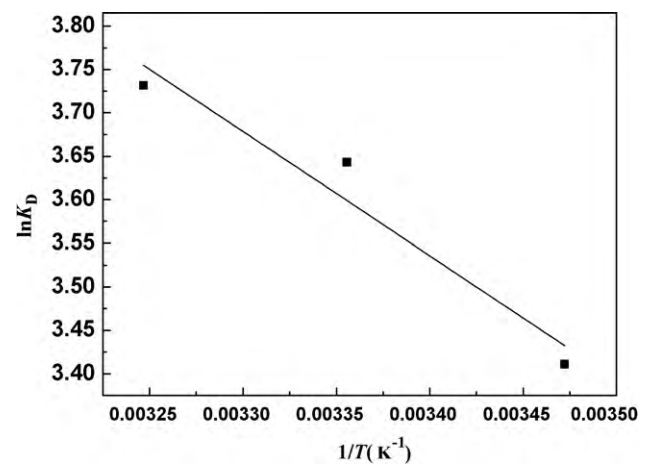


Fig. 6. Plot of $\ln K_D$ vs. $1/T$ for the adsorption of lead onto CSAC.

Thermodynamic parameters of lead(II) adsorption on the CSAC can be evaluated from the variation of the thermodynamic equilibrium constant K_D at different temperature. The adsorption standard enthalpy change and the standard entropy change (ΔS^0) can be calculated plotting of $\ln K_D$ versus $1/T$ according to Eq. (9). The adsorption standard free energy changes (ΔG^0), can be calculated according to Eq. (10).

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0/R}{T} \quad (9)$$

$$\Delta G^0 = -RT \ln K_D \quad (10)$$

where R refers to the universal gas constant, T denotes the different adsorptive Kelvin temperatures. The thermodynamic equilibrium constant K_D is defined as Eq. (11) for adsorptive reactions [43].

$$K_D = \frac{\alpha_s}{\alpha_e} = \frac{\nu_s q_e}{\nu_e C_e} \quad (11)$$

where α_s and α_e refer to the activity of adsorbed lead(II) and the activity of lead(II) in solution at equilibrium, ν_s and ν_e denote the activity coefficient of the adsorbed lead(II) and the lead(II) in solution, respectively. As the lead(II) concentration in the solution decreases and approaches to zero, K_D can be obtained by plotting q_e/C_e versus q_e and extrapolating q_e to zero [44].

Plot of $\ln K_D$ versus $1/T$ for the adsorption of lead(II) onto CSAC is shown in Fig. 6. The obtained thermodynamic parameters are listed in Table 7. It is well known that these parameters can evaluate the orientation and feasibility of the physicochemical adsorptive reac-

Table 7

Thermodynamic data for adsorption of lead(II) onto CSAC evaluated at different temperatures.

T (°C)	ln K _D	ΔG ⁰ (kJ mol ⁻¹)	ΔH ⁰ (kJ mol ⁻¹)	ΔS ⁰ (J mol ⁻¹ K ⁻¹)
15	3.41	-8.17	11.88	69.80
25	3.64	-9.03	11.88	69.80
35	3.73	-9.56	11.88	69.80

tion [43]. The negative adsorption standard free energy changes (ΔG⁰) at all temperatures indicated that the adsorption reaction was a general spontaneous process. The positive value of enthalpy indicated that the adsorption was endothermic, which is consistent with the observation that the adsorption amount increased with increasing temperature. The positive standard entropy changes (ΔS⁰) indicated the increased randomness at the solid liquid interface during the adsorption process, and also suggested the process was entropy driven and not enthalpy driven. The absolute value of Gibbs free energy (ΔG⁰) increased with increasing temperature indicated a higher adsorption impetus in higher temperature.

4. Conclusion

Taguchi method has been used to optimize the conditions of the preparation of AC from cotton stalk for lead(II) adsorption using H₃PO₄ as activator by one-step activation. The cotton stalk activated carbon (CSAC) prepared at the optimized conditions has 1.43 mmol g⁻¹ acidic surface groups and 1570 m² g⁻¹ BET surface area. Pore structure analysis shows its mesoporous character defined by IUPAC. The maximum adsorption capacity of lead(II) was found to be 119 mg g⁻¹ for CSAC at 25 °C. The presence of surface functional oxygen-containing groups proved to be favorable for the adsorption. The adsorption was greatly influenced by solution pH. The equilibrium pH values after adsorption were lower than initial pH values, indicating that the ion-exchange process was involved in the adsorption. Thermodynamic study showed the adsorption was a spontaneous and endothermic process. The value of enthalpy was positive, further indicating that the adsorption was involved in some chemical reactions. The above results showed that the cotton stalk activated carbon prepared by one-step H₃PO₄ activation was a potential adsorbent for adsorptive removal of lead(II) from solution water.

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