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Determination of Arsenic in Soil Alkali by Graphite Furnace Atomic Absorption Spectrophotometery Using Modified Corn Silk Fiber as Adsorbent

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Summary: A safe, rapid, simple and environmentally friendly method based modified corn silk fiber (MC), chemical modified with succinic anhydride ($C_4H_4O_3$),was developed for the extraction and preconcentration of As(Ш)in food additives soil alkali sample prior to graphite furnace atomic absorption spectrometry (GFAAS) analysis. The structure and properties of VC (unmodified corn silk fiber) and MC were analyzed and discussed by means of FTIR, SEM and TG, and the effect of adsorbent amount, pH, soil alkali solution concentration, adsorption time and adsorption temperature were carefully optimized. Under the optimum conditions, the relative standard deviations (RSD, n=6) were1.27-3.05%, the calibration graph was linear in the range of 0-100ug/ L and the limits of detection (LOD) was 0.13μg/L.The surface of MC became loose and porous which increased the adsorption area. Comparing with VC, carboxy groups were measured in MC and the increase of negative electron group in fiber molecular made its coordination combining ability with As(Ш) enhanced; In comparison with the removal arsenic rate of VC, MC's significantly increased by 2.86 fold. The recovery rate of soil alkali, treated by VC and MC, reached to 96.85%and 94.32% ,and it did not affected the function of soil alkali.

Keywords: Modified corn silk fiber; Chemical modified; Succinic anhydride; As(Ш)in food additives soil alkali; Graphite furnace atomic absorption spectrometry analysis;

Introduction

Soil alkali, which was a kind of frequently-used food additives in Yunnan Dali area, consists of 28 elements such as: arsenic, potassium, lead,sodium, fluorine and so on. And the content of arsenic in soil alkali was tested by 2.79~3.87mg/Kg [1]. However World Health Organization stipulated every person intake arsenic content should not exceed 0.3mg/Kg each day [2], so the content of arsenic in soil alkali exceed food additive arsenic levels, and people should strictly limit the popularization and application of soil alkali. Traditional methods for removing arsenic are chemical precipitation (CP) [3], ion exchange (IE) [4, 5], adsorption method (AM) [6, 7], and biological technology (BT) [8]. These are more expensive with poor efficiency and are only applicable at the high arsenic concentrations. When the concentration of arsenic was low the adsorption effect was not obvious.

Recently, in order to search for a way that was very effective, environmentally friendly and low-cost, the researchers tried to use modified fiber to remove arsenic instead of the normally used methods. The armour hydroxyl in fiber molecular could be reaction with chemical reagent which resulted in the introduction of new functional group and enhanced the ability of adsorption ions [9]. Xuejing Yang used natural corncob fiber, pre-processed by Microwave, as raw material which was chemical modified with succinic anhydride. The modified corn silk fibers was produced and used to adsorb Pd(II) from waste water. These results showed that, compared with natural corncob, the maximum adsorption capacity of modified corncob increased more than 5 times, and modified corncob adsorption palladium ion isotherm confirmed to the Langmuir model. The modified corncob still had better adsorption capacity (90%) and recovery capacity (80%) after 4 cycles of use. Due to the mass ratio of corncob and waste water was minimum, so the modified corncob had no impact on other ion in waste water [10]. Compared with the traditional method, the modified fiber as adsorbent was safe, fast, effective, no pollution and had renewable performance.

Owing to precision and ease of operation, graphite furnace atomic absorption spectrometry

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(GFAAS) was a very effective technique for arsenic determinations. Although their concentrations were low in soil alkali sample, it was still very necessary to determine the content of arsenic.

In this study, the natural corn silk fiber(VC),pre-processed by Microwave, were regarded as raw material and chemical modified with succinic anhydride ($C_4H_4O_3$). The modified corn silk fiber MC was produced and used to adsorb As(Ш) in food additives soil alkali. The structure and properties of VC and MC were analyzed and discussed by means of FTIR, SEM and TG, and the effect of adsorbent amount, pH, soil alkali solution concentration and adsorption time were carefully optimized. This research provided a theoretical basis and practical guidance for the study of adsorption of arsenic.

Experimental

Preparation of Materials

Corn silk fibers, through a 100 mesh sieve, were prepared and provided by abandoned agricultural products. It were dried at 55ºC for 1h and kept in a desiccator. Next, corn silk fibers were processed by sodium hydroxide. Succinic anhydride, 0.03g/mL soil alkali solution, sulfasalazine, saturated sodium bicarbonate, nitrate, As(Ш) absorption standard (1. 0μg /ml) were made up.

Apparatus

The microwave oven was used for pretreatment of corn silk fiber. The chemical structure of MC and VC were analyzed in a Infrared spectra in KBr pellets ,enrolled in a Bomem MB-100 FTIR instrument, and dried at a electric air blowing drying box GZX-9140 MBE analysis meter.Contents of As^{3+} were confirmed by graphite furnace atomic adsorption spectrometry(GFAAS) analysis(American PP company Analyst 800).A scanning electron microscope JCM-6000 Neo Scope analyzer, whose spectrum was recorded at14cm resolution with 32co-added scans , was used to distinguish the structure of MC and VC.

Preparation of MC

Samples of 4.3g of corn silk fibers ,through a 100 mesh sieve, were put into the microwave oven with 800W for 2min .Then corn silk fiber were reaction with 81ml pyridine for 1.5h at 90 ºC in a 500ml three necked flask with a mechanical stirrer. 4.3 milliliters of succinic anhydride($C_4H_4O_3$) in glass syringes with stainless steel needles were tardily added into three necked flask,and the reaction system was kept sostenuto stirring and reflux for 2.5h at 90 ℃.We used distilled water and ethanol to wash the production five times.And it was dried in electric air blowing drying box at 60℃for 2h. Scheme-1 showed the process of MC being gained.

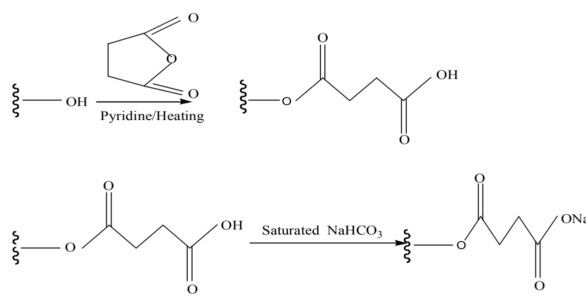


Chart. 1: The preparation route of corn silk modified with succinic anhydride.

As(Ш) adsorption

In order to ensure the content of As(Ш) in soil alkali solution, treated by MC and VC, the adsorption experiments would be performed .The tests were carried out by putting 0.06g of MC or VC and 30mL 0.3g/mL soil alkali solution pour into 100mL beaker with Magnetic stirring for 40min at 25ºC.The concentration of arsenic in soil alkali solution,t reated by VC and MC, was measured by GFAAS. The removal arsenic rate of adsorbents and the rate of recovery of soil alkali were calculated according to the standard working curve and the calculation the arsenic removal rate.

The calculation of the arsenic removal rate by using the standard curve：

$Y=Ac+b_1$,$R^2=0.97\sim1.0$

$W=(v_oc_0-vc)\times100\%/v_oc_0$

Y was the absorbance, A and b_1 were constants, W was the removal arsenic rate, V_O and V were the initial and final soil alkali solution volume (mL).

Results and Discussion

Thermogravimetry Analysis of Adsorbents

Thermal decomposition events were described in Table-1. The data In Table-1 showed the weight of MC and VC had a little of mass loss between 25 and100 ºC. It could be ascribed to loss of moisture [11]. The majority mass weight of MC reduced between 100 and 200 ºC, because the esterfunction was broken [12], producing carbon dioxide and water. The total moss loss ranged of MC Ph 12, pH7 MC and pH4 MC were 47.6%, 42.5%and 38.2%. But the moss of VC had not obvious change at the temperature range of 25~200 ºC.

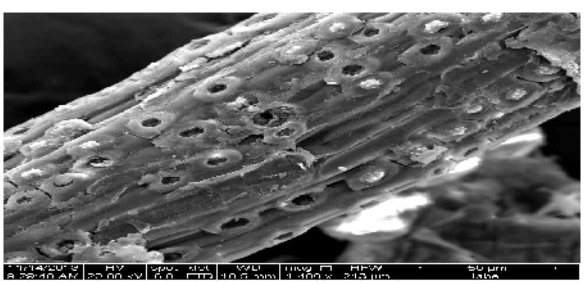
Table-1: Thermal Decomposition Incidents.

	pH	25℃	70℃	100℃	150℃	200℃
VC	4.0	0.721g	0.701g	0.699g	0.690g	0.687g
VC	7.0	0.742g	0.711g	0.710g	0.703g	0.695g
VC	12.0	0.751g	0.702g	0.696g	0.689g	0.681g
MC	4.0	0.681g	0.613g	0.609g	0.602g	0.420g
MC	7.0	0.741g	0.704g	0.697g	0.580g	0.426g
MC	12.0	0.690g	0.631g	0.628g	0.532g	0.365g

SEM Observations of the Fibers

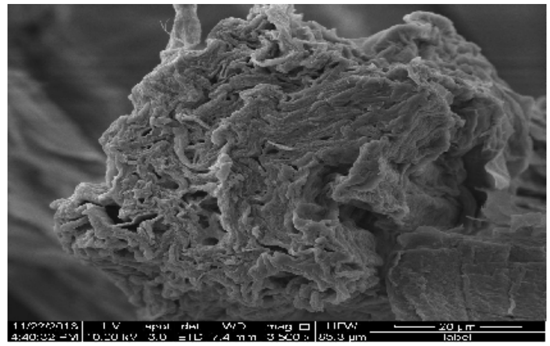
The Fig. 1 and Fig 2 showed the SEM pictures of MC and VC. For VC, Celluloses were a closely integrated and wrapped together, and the surface structure was compact. A groove appeared on the surface of fibers, but the surface of the groove was smooth. However, for MC, although its appearance was still can keep the original structure, the morphology was packed more and looser. Some gully cracks and holes were observed on the surface of the original grooves, and the surface of gully was wide. This phenomenon increased adsorption surface area and enhanced adsorption As(Ш) ability.

a1(×1400)

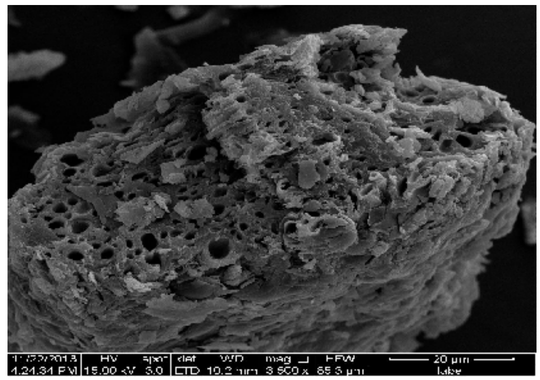


b1(×1400)

Fig. 1: SEM spectra of MC(a) and VC(b) (×1400).



a2(×3500)



b2(×3500)

Fig. 2: SEM spectra of MC(a) and VC(b) (×3500).

FTIR Spectra of the Fibers

Fig 3 showed the FTIR spectra of MC and VC. In the FTIR spectrum of MC, the IR spectra had peaks at ca.1650-1700cm^{-1} which was attributed to the C=O stretching and 2700-30000cm^{-1} which correspond to the ester C=O stretching vibration and carboxylic acid O-H [13].while the wide bands at 1650-1700cm^{-1}and 2700-3000cm^{-1} for VC had not peaks, further meaning the efficacious coupling of the needful function to the material. The result showed that there was no carboxyl based in VC, and the corn silk fiber and citric acid chemical reaction occurred, introducing new functional group.

Analytical Features

Under the optimum conditions, the relative standard deviations (RSD, n=6) were 1.27–3.05%,the calibration graph was linear in the range of 0-100ug L^{-1}and the limits of detection (LOD) was0.13μg/L,the regression equation was Y=0.00341c+0.0075, R^2=0.9719.The results were shown in Table-2.

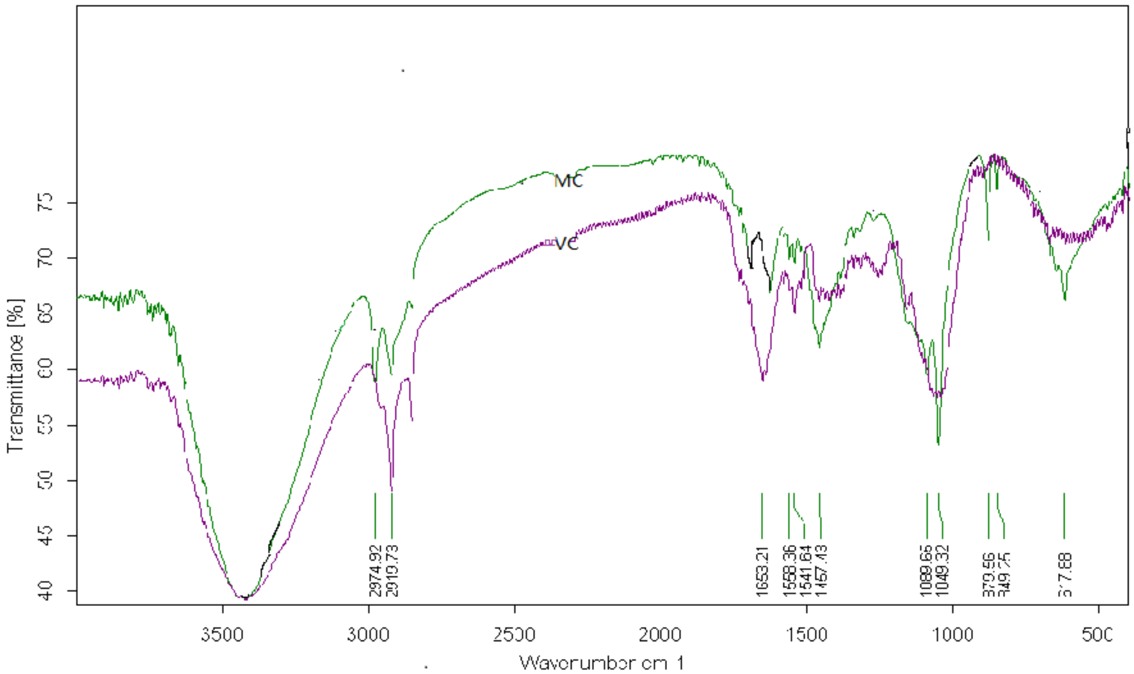


Fig. 3: Infrared spectra of the fibers in KBr pellet.

Effect of Soil Alkali Solution Concentration

Different soil alkali solution concentrations of 30mL and 0.07g pH7 MC or pH7 VC were added into some beakers at 50 ºC, and the adsorption time was 40min. This experiment mainly studied the soil alkali solution concentration range of 0.05~0.3g/mL affected the adsorption As (III) effect. Fig 4 showed that the adsorption capacity and the removal arsenic rate of MC and VC increased with soil alkali concentration increasing. This phenomenon may be due to soil alkali solution concentration was high, and As(III) gathered in the adsorbent surface more easily and the adsorption capacity increased. In this experiment, the best soil alkali solution concentration was 0.3g/mL, compared with VC control group; the removal arsenic rate of MC was significantly increased 2.62 times.

Effect of the Adsorption Time

When the adsorption As(Ш)procedure was processed at the equilibration time of the surfactant, the best extraction efficiency was achieved. This experiment mainly studied the adsorption time range of 0~60min affected the adsorption As (III) effect. According to the Fig5 ,we would known that the removal arsenic rate of MC and VC increased with increasing time at time range of 0~40min,while the removal arsenic had no change from 40 to 60min.It because a large number of high As(III) concentrations gathered at the surface of adsorbent in the initial stage of the reaction , but the surface quantity, contacted with As (III) ,would reached saturation with the increase of reaction time. The best adsorption time was 40 min. Compared with VC, the removal arsenic rate of MC was significantly increased 2.81 times .

Effect of Adsorbents pH

Because fiber may produced three pKa values at ca. 3.9,7.1and 11.6,tallying with the reported pKa values of oxalic acids, polysaccharide [14] and phenols [15] current in fiber materials, so pH of MC and VC may affected the adsorption As (III) effect. This experiment mainly studied the pKa value of adsorbents range of 2~7 .The results were displayed in Fig6.The removal arsenic rate at pH range of 2~7 increased with increasing pH, and the removal arsenic rate reduced with reducing from pH7 to 14.This phenomenon may be because acidic and alkaline fiber had an impact on elements in soil alkali, such as: arsenic, lead and fluorine which produced easily stable compounds with H^+ or OH^-. And It affected the adsorption As (III) effect. So pH7 was the best pKa value. Compared with VC, the removal arsenic rate of MC was significantly increased 2.65 times.

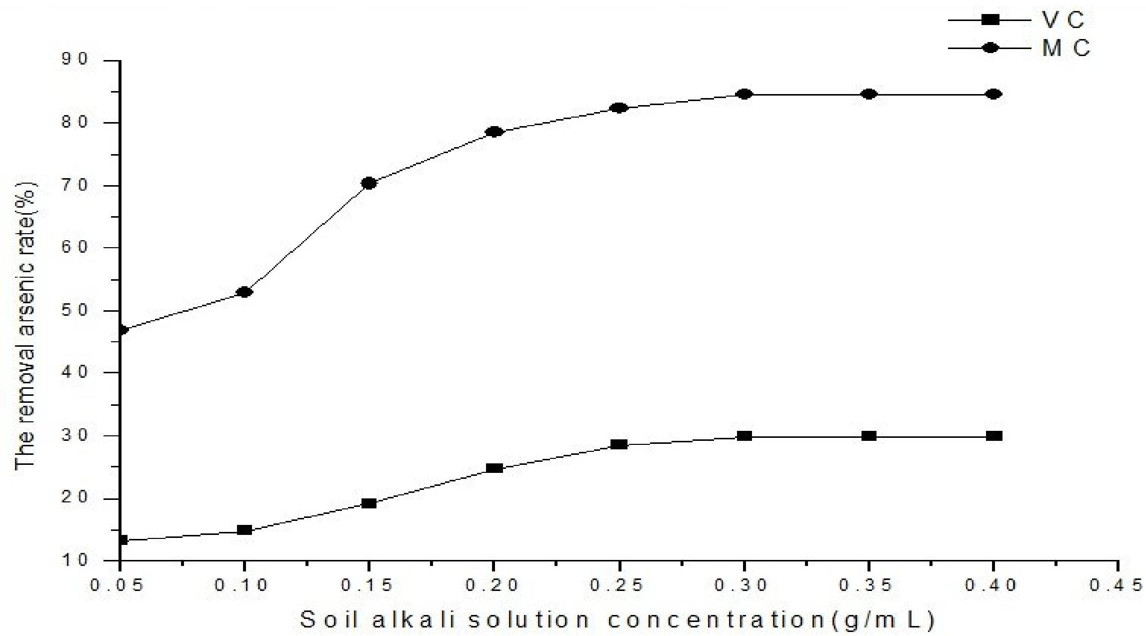


Fig.4: Effect of soil alkali solution concentration. Experimental condition: 0.07g pH7 MC or pH7 VC, t=40min and T=50ºC. Other experimental conditions were described procedures.

Table-2: Performance characteristics of the proposed method.

Analyte	Linear range(μg/mL)	Regression equation	R^2	LOD(μg/L)	RSD(%)n=6
As	0-100	Y=0.00341c+0.0075	0.9719	0.13	1.27-3.05

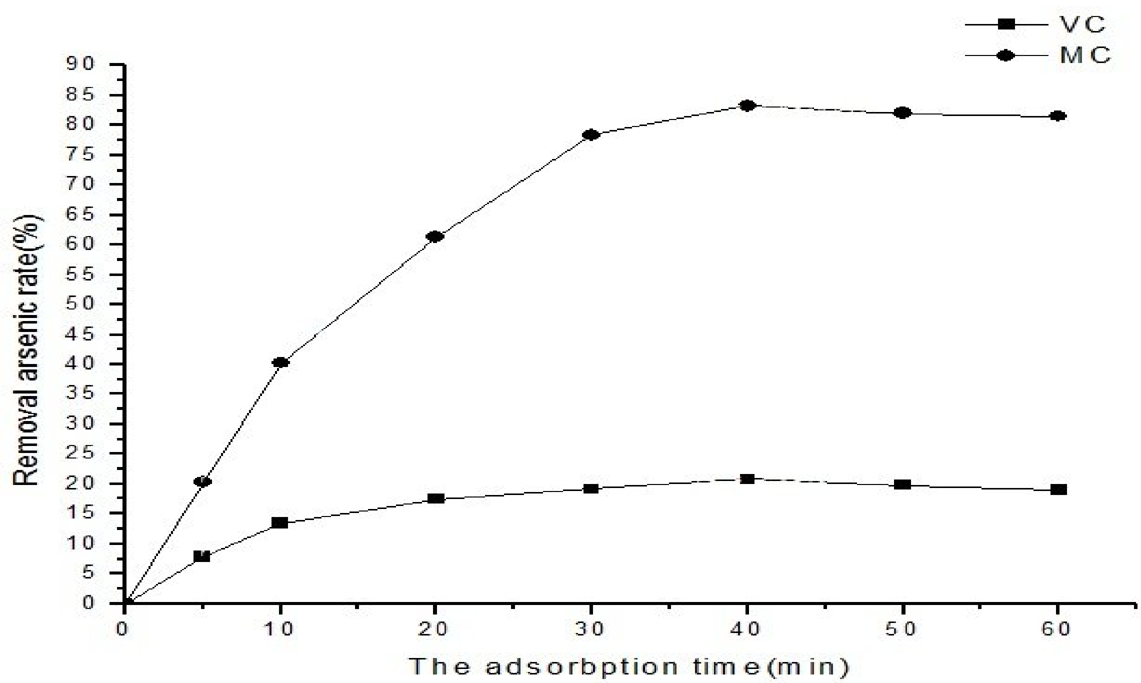


Fig. 5: Effect of the adsorption time. Experimental condition:30mL 0.3g/mL of soil alkali ,0.07g pH7 MC or pH7 VC,T=50 ºC.Other experimental conditions were described procedures.

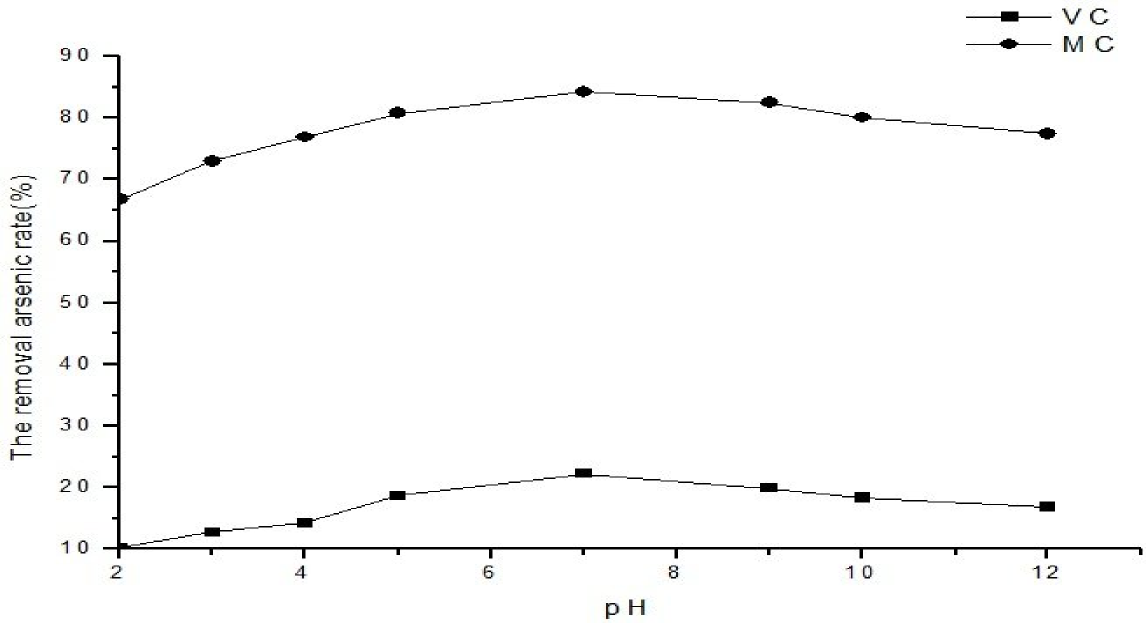


Fig.6: Effect of pH. Experimental condition: 30mL 0.3g/mL of soil alkali, t=40min and T=50℃. Other experimental conditions were described procedures.

Effect of the Adsorption Temperature

As we all know, the temperature affected the molecular motion. The molecular motion was very intense when the temperature build-up. But because of some influence factors, such as environmental temperature, molecular motion range, and interactions between the molecules, the adsorption amount would reach saturation at a certain temperature which was the equilibration temperature. 30mL 0.3g/mL soil alkali solution and 0.07g pH7 MC or pH7 VC were added into some beakers at difference temperature, and the adsorption time was 40min. This experiment mainly studied the adsorption temperature range of 25~60 ºC affected the adsorption As (III) effect.

It can be seen from Fig7, at a temperature of 25~50 ºC, the removal arsenic rate increased with increasing adsorption temperature, while the adsorption reached saturation at adsorption temperature range of 50~60 ºC. So this study choose 50 ºC as adsorption equilibration temperature. Compared with the control group VC, the removal arsenic rate of MC was increased by 2.29 times, because the electrically negative group and carbonyl parathion were introduced for MC which could increased adsorption As (III) of the fiber .

Effect of the Amount of Adsorbent

When the adsorption As(Ш)procedure was processed at the equilibration amount of the surfactant, the best extraction efficiency was achieved. This experiment mainly studied the amount of adsorbents range of 0.01~0.1g affected the adsorption arsenic (III) effect. The Fig. 8 showed that the removal arsenic rate of VC and MC at weight range of 0.01~0.07gincreased with increasing weight. While the adsorption reached saturation at adsorbent dosage range of 0.07~1.0g.Although adsorbent dosage increasing can increased the adsorption surface area, the concentration of As(III) in soil alkali solution became low with increasing the adsorption time, and it was very difficult to adsorbing As (III) .So 0.06g was the best adsorbent dosage. Compared with VC, the removal arsenic rate of MC was significantly increased 2.86times .The recovery rate of soil alkali, treated by VC and MC,reached to 96.85%and 94.32% .

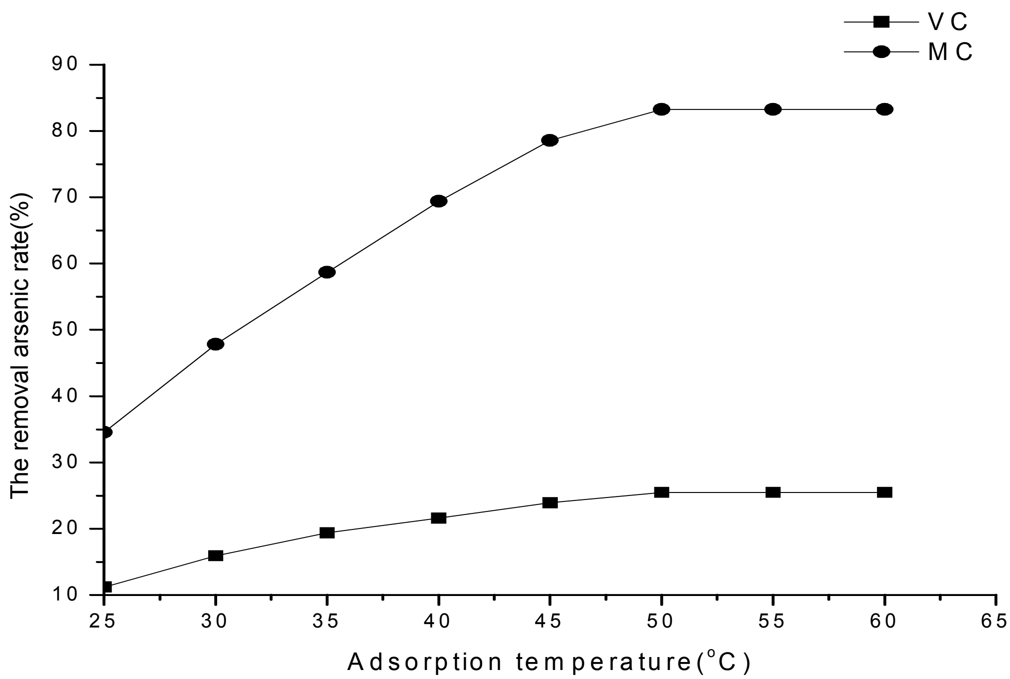


Fig.7: Effect of the adsorption temperature. Experimental condition: 30mL 0.3g/mL of soil alkali, t=40minand 0.07g pH7 MC or pH7 VC. Other experimental conditions were described procedures.

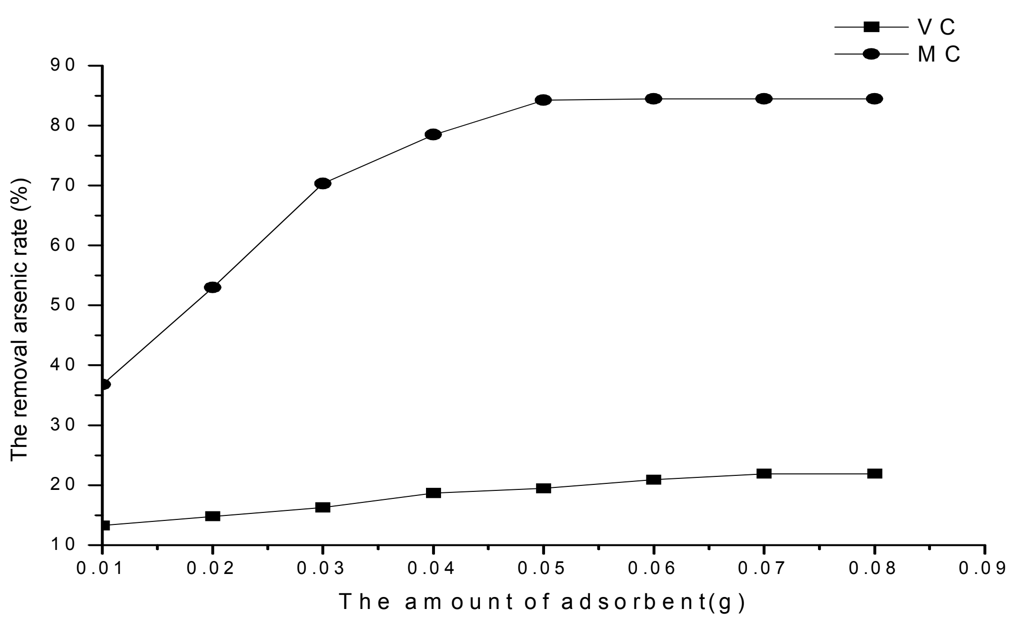


Fig.8: Effect of the amount of adsorbent. Experimental condition:0.07g pH7 MC or pH7 VC,30mL 0.3g/mL of soil alkali, t=40min and T=50 ºC.Other experimental conditions were described procedures.

The Adsorption Type

The activation energy size could reflected the adsorption type. The activation energy of Physical adsorption was generally not more than 4.2 kJ/mol. Due to the chemical adsorption may produced new compounds, so it needed higher activation energy, and the chemical adsorption activation energy range was 40~100 kJ/mol.

The calculation activation energy equation of Arrhenius [16]:

$$K=A_f e^{-Ea/RT}$$

A_f was the frequency factor ($4.2\times10^8 kg\cdot mg^{-1}\cdot min^{-1}$); T was temperature (K); R was the gas constant ($8.314 J\cdot mol^{-1}\cdot K^{-1}$), Ea was the activation energy ($kJ\cdot mol^{-1}$). Equation can be changed into:

$$\ln k=\ln A_f - Ea/RT$$

Adsorption rate constants K and T=289K were used to calculate the activation energies of VC and MC adsorption process. And they were respectively $37.24 kJ\cdot mol^{-1}$ and $55.67\ kJ\cdot mol^{-1}$, indicating that VC adsorbing As (III) in food additives soil alkali was physical adsorption, while MC adsorbing As (III) was mainly chemical adsorption. The equations of VC and MC on lnK and 1/T were got, and they were lnk=-4479.2/T+19.85 and lnk=-6694.1/T+19.85, respectively.

Adsorption Isotherms Modeling

At a constant temperature,for a monolayer coverage of the adsorbent,the Langmuir adsorption model was frequently used as a method to depict absorptivity and adsorbate-adsorbent equilibrium (Langmuir,1918) [17]:

$$\frac{1}{q_e}=\frac{1}{c_e b q_{max}}+\frac{1}{q_{max}}$$

where c_e was the equilibrium concentration of solution (μg/mL)and q_e was the equilibrium adsorption capacity (μg/mg);q_{max} was the theoretical maximum saturated adsorption capacity; b,which was Langmuir constants, associated with the affinity binding site.

Langmuir adsorption isotherm could clearly describe the relationship between equilibrium concentration and equilibrium adsorption capacity in Table-3. We often used the constant b to indicate the degree of difficulty of the adsorption reaction. In this experiment, because Ce (g/mL) was greater than1.0, when b was in the range of 0~1.0the adsorption reaction easily carried out; On the other hand, the adsorption reaction was difficult to carry out when b was grater than 1.0. b in the experimental was both less than 1.0, so the adsorption reaction could be carried out smoothly. And the bigger the b value, the adsorption capacity was strong. The adsorption isotherm of VC and MC adsorbing As (III) accorded with the Langmuir model.

Table-3 Langmuir parameters for As^{3+} adsorption in the different adsorbents (pH=7, 25℃).

Adsorbents	Langmuir equation	q_{max}(mg/g)	b	R^2
VC	$C_e/q_e=1.062C_e+1.002$	0.942	0.9634	0.9805
MC	$C_e/q_e=0.281C_e+12.538$	3.559	0.0224	0.9779

Conclusion

In this experiment, the natural corn silk fiber, pre-processed by Microwave, were regarded as raw material and chemical modified with succinic anhydride($C_4H_4O_3$).The modified corn silk fiber was used to adsorb As(Ш) in food additives soil alkali. Some results would be obtained:

1) Under the optimum conditions, the relative standard deviations (RSD, n=6) were1.27–3.05%, the calibration graph was linear in the range of 0-100ug $L^{-1}$and the limits of detection (LOD) was 0.13μg/L,respectively.
2) The surface of MC became loose and porous which increased the adsorption area. Comparison with VC, carboxy groups were measured in MC, and the increase of negative electron group in fiber molecular made its coordination combining ability with As(Ш) enhanced;
3) The optimum technological conditions of the modified fiber adsorbing arsenic:adsorption time was 40min,adsorption temperature was 50 ℃,pH=7;In comparison with VC,the removal arsenic rate of MC significantly increased by 2.86fold.The recovery rate of soil alkali, treated by VC and MC, reached to 96.85% and 94.32% .
4) Adsorption type of unmodified fiber adsorbing As(III) in food additives soil alkali was physical adsorption, while adsorption type of modified fiber adsorbing As(III) was main chemical adsorption; The adsorption isotherm of corn silk fiber adsorbing As(III) conformed to Langmuir

adsorption model.

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