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Study on Crosslinked Chitosan Adsorbent of Heavy Metals in Traditional Chinese Medicine

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This study investigated the adsorption effect in which the composite adsorbent [CTS-Fe(II)] was crosslinked by different molecular weight chitosan and ferrous ammonium sulfate. We tested effect of adsorption in traditional Chinese medicine *i.e.*, Chuanxiong contained harmful elements such as lead, cadmium by atomic absorption spectrometry, tested adsorption effect of tetramethylpyrazine using CTS-Fe(II) by UV, we also explored the impact of the temperature, amount and time on the adsorption. The results showed that CTS-Fe(II) composite adsorbent used in the process, adsorbent dosage was 0.36 g, the adsorption temperature was 25 °C, time was 120 min, the maximum absorption amounts of CTS-Fe(II) on heavy metal were more than 90 %, the retention amounts of the active ingredient were 70 %, so CTS-Fe(II) was a good adsorbent for handling herbs.

Keywords: Chitosan, Ferrous ammonium sulfate, Heavy metals, Chuanxiong.

INTRODUCTION

There are two main sources of heavy metals in traditional Chinese medicine, one is for therapeutic purposes, in prescriptions added mineral drugs containing heavy metals, such as cinnabar and realgar. The second is by the quality of raw materials or in its processing, storage, transportation and preparation of the production process, which is exogenous contamination. These two sources cause excessive levels of heavy metals in traditional Chinese medicine. It becomes one of medicine safety issues in the international community, which hinder the process of internationalization of Chinese medicine. For non-prescription of heavy metal pollution, we should strictly controlled in order to avoid heavy metals weakening effects of drug treatment and causing physical harm to the user. Heavy metals in herbs are related to cultivated way, the content of heavy metals in herbs is related to the content of heavy metals in the soil. For example, lead is widely distributed in nature, plants can absorb lead through the roots from the soil, processing machinery and equipment, piping *etc*. also contained lead, lead is mainly in the kidney, spleen, lung, brain, especially in the liver[1].

Now most of Chinese medicine products need to be green certification, ministry of commerce promulgate the "medicinal plants and preparation of foreign trade green industry standard" provisions of medicinal plants and preparation of foreign trade industry standard quality, which include herbal pieces, extracts and pharmacy[2]. The data of heavy metals limit requirements is shown in Table-1.

Chitosan (CTS), is natural polymers extract from the shell of crustaceans, with non-toxic, inexpensive, can be biodegradable and good adsorption properties. Chitosan molecules which belong to alkaline polysaccharide have free amino group, as the molecular chain have the amino and hydroxy, derivative reaction will occur[3-5]. Chitosan is a natural cationic flocculant which has chelating adsorption for many substances. In its molecule there are an amino group and an adjacent hydroxyl group with many metal ions to form stable chelates, so this can be used to deal with wastewater containing heavy metals[6].

TABLE-1
HEAVY METALS LIMIT REQUIREMENTS

Heavy metal	Symbol	Content (mg/kg)
Total heavy metals	≤	20
Lead	≤	5.0
Cadmium	≤	0.3
Copper	≤	20.0

The main components of Chuanxiong are tetramethylpyrazine and ferulic acid. The pharmacological effects of Chuanxiong are blood circulation and expelling wind pain[7], it is widely used in Chinese medicine products.

This study investigate the chitosan crosslinked ammonium ferrous sulfate in order to achieve good results for the adsorption of heavy metals and retain the active ingredient in Chinese herbal medicines and related beneficial elements.

EXPERIMENTAL

Chitosan (CTS_1): DAG ≥ 85 %, 200CPS molecular weight 120,000 to 130,000, Jinan Hyderabad Marine Biological Engineering Co., Ltd.; Chitosan (CTS_2): DAG ≥ 92 %, 27CPS, Shandong Haili Biological Products Co., Ltd.; Chitosan (CTS_3): DAG = 90 %, Jinan Hyderabad Marine Biological Engineering Co., Ltd.; coal ash, cadmium nitrate, lead nitrate, ammonium ferrous sulfate, sodium hydroxide; acetic acid, hydrochloric acid, nitric acid, sulfuric acid are CP grade, anhydrous copper sulfate, methanol, ethanol, isopropanol are AR grade, Beijing reagent Factory. Ligustrazine hydrochloride, National institutes for food and drug control.

361MC atomic absorption spectrophotometer Shanghai Precision Instrument Co., Ltd., 723PC UV spectrophotometer Shanghai Tempe Analytical Instrument Co.

Preparation of crosslinked chitosan

Preparation of CTS-Fe(II): Ferrous ammonium sulfate is weighed 23.5 g, dissolved in 250 mL boiled deionized water, place with 1 mol/L hydrochloric acid to adjust pH 2-3; add CTS 0.5 g, stirrer, the reaction left for 3 h then filtration. The filtrate is added an equal volume of anhydrous ethanol and allowed to stand for 12 h, until the product precipitated is filtered, washed with 50 % ethanol, dry in 40 °C oven.

Preparation of CTS-carbon: Take 20 g coal ash, adding 0.16 g of chitosan mixed homogeneously and then adding 4 % acetic acid 12 mL, sufficiently stirred to prepare a paste, completely wet, having a diameter of 1-3 mm small particles and drying.

Preparation of extract of chuanxiong: Weigh chuanxiong 160 g, add 800 mL 70 % ethanol and reflux 2 h, repeat the extraction three times, filter, combined extracts, using a rotary evaporator and concentrated to 200 mL.

Analytical method: UV analysis is applied to determine the content of ligustrazine hydrochloride. Dissolve 18.1 mg ligustrazine hydrochloride in 10 mL water, then separately weigh 0.4, 0.6, 0.8, 1.0, 1.2 mL solution and dilute with water to 10 mL, ligustrazine hydrochloride is calculated using the standard sample as the calibration standard. A good linear relationship is obtained over the range of 2.7784×10^{-2} μg/mL < C < 8.3262×10^{-2} μg/mL and the regression is y = 0.098x + 0.067 (R = 0.9998), where y is the absorbance at 299 nm, x is the concentration of ligustrazine hydrochloride (10^{-2} μg mL^{-1}) and R is the regression coefficient.

Atomic absorption spectrometry is applied to determine the content of heavy metals. Flame atomic absorption instrument parameters are shown in Table-2.

TABLE-2
FLAME ATOMIC ABSORPTION INSTRUMENT PARAMETERS

	Cd	Pb
Detection wavelength/nm	228.8	283.3
Slit width/mm	0.4	0.4
Lamp Current/mA	3	3
Drying temperature/°C	100	100
Atomization temperature/°C	2000	2400

Standard solution of lead(II): 0.160 g lead nitrate is dissolved in 10 mL nitric acid, then transferred to 1000 mL volumetric flask and diluted to volume with water.

Standard solution of cadmium(II): 0.203 g cadmium chloride is dissolved by water in 1000 mL volumetric flask and diluted to volume with water.

Standard curve equation and parameters are shown in Table-3.

TABLE-3
STANDARD CURVE EQUATION AND THE REGRESSION COEFFICIENT

Measured elements	Standard curve equation C (μg/mL)	Regression coefficient
Pb	A = 0.0044C – 0.0013	0.9967
Cd	A = 0.0496C + 0.0155	0.9946
Linear range: 0 ≤ C ≤ 10 μg/mL		

RESULTS AND DISCUSSION

Effect of adsorption with different crosslinked chitosan: Weighed six kinds of prepared chitosan 0.14 g, respectively, put them in six 100 mL extract of chuanxiong, respectively then Erlenmeyer flasks are placed in water bath at 37 °C, adsorption 90 min, filter, the filtrate was analyzed by UV. The adsorption data which six kinds of chitosan crosslinked adsorbents adsorb active ingredients ligustrazine is shown in Table-4.

TABLE-4
DATA OF CHITOSAN CROSSLINKED ADSORB LIGUSTRAZINE

Adsorbent species	Concentration of ligustrazine (μg/mL)
CTS_1-Fe (II)	14.6224
CTS_2-Fe (II)	14.6633
CTS_3-Fe (II)	16.9286
CTS_1-coal ash	9.1224
CTS_2-coal ash	6.0102
CTS_3-coal ash	6.4489
No adsorbent	17.2448

CTS- coal ash adsorbent for the adsorption of ligustrazine is a very serious, even if this type of adsorbent have a good effect on adsorption of heavy metals, but the active ingredients in herbs will lose a lot, so CTS-coal ash does not apply to Chinese medicine production. Compare with CTS-Fe(II) adsorbent, deacetylation degree (90 %) CTS_3-Fe(II), adsorption of ligustrazine is the least, adsorption capacity descending order is CTS_1-Fe(II) > CTS_2-Fe(II) > CTS_3-Fe(II).

Weighed CTS_1-Fe(II), CTS_2-Fe(II) and CTS_3-Fe(II) 0.14 g respectively, put them in three 100 mL waste water which contain heavy metals, respectively, then Erlenmeyer flasks are placed in water bath at 37 °C, adsorption 90 min, filter, the filtrate was analyzed by atomic absorption spectrometry. The adsorption data which three kinds of chitosan crosslinked adsorbents adsorb heavy metals is shown in Table-5.

Table-5 showed the comparison of three chitosan crosslinked adsorbents, CTS_1-Fe (II) and CTS_2-Fe (II) have strong adsorption capacity of heavy metals, considering adsorption capacity of less the active ingredients in herbs and more heavy metals, we choose CTS_2-Fe(II) for further study.

Experiment of the influencing factor in CTS_2-Fe(II) adsorb heavy metals: The orthogonal table is designed according to three factors and three levels. Three variables are

TABLE-5
DATA OF CHITOSAN CROSSLINKED ADSORPTION OF HEAVY METALS

Adsorbent species	Lead		Cadmium	
	Amount of Pb in solution (μg)	Adsorption rate (%)	Amount of Cd in solution (μg)	Adsorption rate (%)
CTS_1-Fe(II)	4.9000	56.6	2.6915	15.5
CTS_2-Fe(II)	5.3000	53.1	2.5907	18.7
CTS_3-Fe(II)	5.4250	52.0	2.7721	13.0
Waste water	11.3021	-	3.1863	-

temperature, the amount of adsorbent CTS_2-Fe(II) and adsorption time. Three factors and three levels orthogonal experiment is shown in Table-6, the results of orthogonal test are shown in Tables 7 and 8.

TABLE-6
3 LEVELS AND 3 FACTORS GRAPH

Level	Amount of adsorbent (g)	Adsorption time (min)	Temperature (°C)
1	0.28	60	25
2	0.20	90	37
3	0.36	120	50

TABLE-7
RESULTS AND CALCULATIONS OF ADSORBING LEAD(II)

Test	Amount of adsorbent (g)	Adsorption time (min)	Temperature (°C)	Adsorption rate (%)
1	0.28	60	25	61.16
2	0.28	90	50	18.47
3	0.28	120	37	57.69
4	0.20	60	50	39.24
5	0.20	90	37	49.31
6	0.20	120	25	45.77
7	0.36	60	37	38.47
8	0.36	90	25	90.00
9	0.36	120	50	56.93
K1	45.77	46.29	65.64	
K2	44.77	52.59	48.49	
K3	61.80	53.46	38.21	
R	17.03	7.17	27.43	

TABLE-8
RESULTS AND CALCULATIONS OF ADSORBING CADMIUM(II)

Test	Amount of adsorbent (g)	Adsorption time (min)	Temperature (°C)	Adsorption rate (%)
1	0.28	60	25	68.84
2	0.28	90	50	63.62
3	0.28	120	37	85.75
4	0.20	60	50	93.00
5	0.20	90	37	88.33
6	0.20	120	25	86.97
7	0.36	60	37	81.81
8	0.36	90	25	95.00
9	0.36	120	50	87.65
K1	72.74	81.22	83.60	
K2	89.43	82.32	85.30	
K3	88.15	86.79	81.42	
R	15.42	5.57	3.87	

For adsorbing heavy metal Pb, we can see from Table-7, temperature has remarkable effect on the adsorption rate, the effect of adsorption time on the adsorption rate is the least significant. The optimal experimental conditions are the amount of adsorbent 0.36 g, adsorption time 120 min, temperature 25 °C. For adsorbing heavy metal Cd, we can see from Table-8, the amount of adsorbent has remarkable effect on the adsorption rate, the effect of temperature on the adsorption rate is the least significant. The optimal experimental conditions are the amount of adsorbent 0.20 g, adsorption time 120 min, temperature 37 °C.

Comprehensive analysis of the experimental results, the optimal experimental conditions are the amount of adsorbent 0.36 g, adsorption time 120 min, temperature 25 °C, the adsorption rate of Pb and Cd can reach more than 90 %.

Conclusion

The composite adsorbent [CTS-Fe(III)] was crosslinked by chitosan and ferrous ammonium sulfate. It is an amorphous, yellow-brown powdered solid, neutral in water and insoluble in ethanol, ether and other organic solvents. The adsorption properties of [CTS-Fe(II)] is basically the same with coal ash, the process of production is simple, the yield is high. This adsorbent can repairing heavy metal pollution as an accelerator for soil improvement and do not pollute the environment also.

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