Preparation and Adsorption Properties of Chemically Modified Isatis Indigotica Fort Draff based Biosorbent

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Keywords: Radix Isatidis Residue, Chemical Modification, Adsorbent, Heavy Metals, Removal.

Abstract: Objective: to treat the Isatis Indigotica fort draff to enhance its adsorption capacity for heavy metals. Methods: Isatis Indigotica fort draff was modified with NaOH, Na_2CO_3 and citric acid to prepare Isatis Indigotica fort draff based biosorbent; the structure was characterized by scanning electron microscopy and Fourier transform infrared spectroscopy; then the effects of solution pH value, solution concentration, adsorbent dosage, and adsorption time of copper ion solution on the adsorption performance of Isatis Indigotica fort draff based adsorbent were studied by static adsorption experiments, so as to clarify the adsorption mechanism; it provides a guide for the resource utilization of Isatis Indigotica fort draff and an experimental basis for the preparation of new adsorbents. Results: The adsorption properties of RIR-NaOH, RIR-Na_2CO_3, and RIR-CA were all better than RIR; the order of the maximum adsorption capacity of the modified Isatis Indigotica fort draff based adsorbent for copper ions is: RIR-Na_2CO_3 > RIR-NaOH > RIR-CA > RIR. Conclusion: The Isatis Indigotica fort draff based adsorbent has the potential to remove heavy metals from water, and is a new type of adsorbent.

1 INTRODUCTION

With the acceleration of urbanization and the increase of industrialization, heavy metal pollution in water has gradually become a serious problem that plagues many countries around the world (Bai 2015, Broaga 2014). Heavy metals exist stably and persistently in the environment and accumulate in the human body through the food chain, causing serious harm to human health and ecosystem (Cao 2016, Chen 2010). Therefore, the removal of heavy metals from water is of great significance to both human beings and ecosystems. At present, the main methods to remove heavy metals from wastewater are ion exchange, chemical precipitation, and membrane filtration. However, the wide application of these methods in commercial applications is limited by high cost and low reusability. On the contrary, biosorption has attracted more and more attention in the removal of heavy metals because of its operability and low cost. Biosorbent resources are extensive and easy to obtain, such as algae residue (Dai 2019), herb residue (Deng 2018), and so on. As a Chinese herbal medicine with multiple functions, Radix Isatidis can not only be used for the treatment of some diseases such as influenza (Du 2019), but also for the prevention of diseases (Duan 2021, Huang 2015, Huang 2020, Jia 2016). Radix Isatidis contains a variety of active substances (Jia 2010), which are currently being extensively studied, developed and utilized. Through processing, a variety of Radix Isatidis products can be synthesized (Jiang 2020), such as Radix Isatidis granules, Radix Isatidis injection, and so on. However, if the Isatis Indigotica fort draff after extraction is not treated in time, it will pollute the environment to some extent. Therefore, how to treat the waste Isatis Indigotica fort draff and reduce its pollution to the environment has become an important problem to be solved.

After the active substances are extracted from Radix Isatidis, the drug residue still contains many effective components such as lignocellulose (Kim 2003, Kommula 2013), so the preparation of Isatis Indigotica fort draff into a cellulose based adsorbent is a common treatment method (Pan 2018, Reddy

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Yin, X., Li, J., Zhang, N., Zhu, H., Ke, T., Gu, Y., Meng, J., Wu, J. and Wang, Y.
Preparation and Adsorption Properties of Chemically Modified Isatis Indigotica Fort Draff based Biosorbent.
DOI: 10.5220/0011375600003443
In *Proceedings of the 4th International Conference on Biomedical Engineering and Bioinformatics (ICBEB 2022)*, pages 1013-1021
ISBN: 978-989-758-595-1

2019). Lignocellulose is composed of carbohydrates (cellulose and hemicellulose), lignin, and other components (protein, lipid and inorganics) (Tan 2019). It is a rich and renewable resource on earth and a good source of heavy metal adsorbents (Tan 2020, Tian 2020, Ulfa 2019, Wang 2019, Wang 2019). However, due to the close connection among the components of lignocellulose, the adsorption of heavy metals by cellulose is hindered. Therefore, the direct use of Isatis Indigotica fort draff for heavy metal adsorption has the problem of low adsorption capacity and adsorption rate. Reasonable modification of Isatis Indigotica fort draff to remove hemicellulose and lignin is very important to increase its adsorption capacity.

In this work, chemical reagent was used to modify Isatis Indigotica fort draff. The structure of resulting absorbent was characterized by scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR). The effects of solution pH value, solution concentration, adsorbent dosage, and adsorption time of copper ion solution on the adsorption performance of Isatis Indigotica fort draff based adsorbent were studied through static adsorption experiment to clarify the adsorption mechanism. It provides guidance for the resource utilization of Isatis Indigotica fort draff and experimental basis for the preparation of new adsorbents.

2 EXPERIMENTAL METHODS

2.1 Materials

The Radix Isatidis used in the experiment came from Huirentang Pharmacy in Lanzhou, and the experimental water was deionized water.

2.2 Methods

2.2.1 Preparation of the Absorbent

(1) Decolorization: The purchased Radix Isatidis was washed with deionized water for 1-2 times, boiled for 3 times (30 min each time), dried at 65 °C, crushed and passed through a 40-mesh sieve. The prepared drug residue and methanol were mixed in a ratio of 1:5 and stirred to remove bioactive components and pigments. The methanol is constantly replaced during stirring until the methanol is colorless after stirring. After washing with distilled water and drying at 65 °C, the prepared drug residue was named as decolorized Isatis Indigotica fort draff and recorded as RIR.

(2) Modification:

1) NaOH modification: The RIR was added into an aqueous solution of NaOH (1 mol/L) at a solid-to-liquid ratio of 10:1 and stirred magnetically for 4 h (120 r/min). The resulting residue was washed with deionized water to be neutral, filtered, and dried, which was named as NaOH modified Isatis Indigotica fort draff and denoted as RIR-NaOH.

2) Na2CO3 modification: The RIR was added into an aqueous solution of Na_2CO_3 (1 mol/L) at a solid-to-liquid ratio of 10:1 and stirred magnetically for 4 h (120 r/min). The resulting residue was washed with deionized water to be neutral, filtered with sand filter funnel, and dried, which was named as Na_2CO_3 modified Isatis Indigotica fort draff and denoted as RIR-Na_2CO_3.

3) Citric acid modification: The RIR was firstly treated with 0.1 mol/L NaOH for 30 min. The resulting residue was then mixed with an aqueous solution of citric acid (0.6 mol/L) at a solid-to-liquid ratio of 10:1 and stirred magnetically for 4 h (120 r/min). The resulting residue was washed with deionized water to be neutral, filtered, and dried, which was named as citric acid modified Isatis Indigotica fort draff and denoted as RIR-CA. All the Isatis Indigotica fort draff based biosorbents were named RIR-Ts.

2.2.2 Structural Characterization of RIR-Ts

(1) FTIR: Fourier transform infrared spectroscopy (FTIR, Nicolet Nexus, USA) was used to study the molecular structure and chemical bonds of RIR-Ts. The samples for analysis were dried before use, ground in a mortar, mixed with potassium bromide powder and pressed into transparent sheets. The experiment was carried out in the spectral range of 4000-400 cm-1.

(2) SEM: the morphology of lignocellulose compounds was studied by SEM (JSM-6701F, JEOL, Japan). The samples for analysis were stored in an oven at 50 ℃ overnight.

(3) analyzer (Perkin-Elmer Cetus Instruments, Norwalk, CT) was used to study the thermal stability and composition of the adsorbent. About 10 mg of the sample was placed in the sample holder and heated from room temperature to 800℃ (heating rate = 10 ℃/min). The purging gas was nitrogen with a flow rate of 20 mL/min.

(4) XRD: the crystalline properties of cellulose were studied by using X-ray diffractometer (JDX-3530,2kw, Tokyo, Japan). Before analysis, the

sample was ground into fine and uniform powder and stored in an oven at 50 °C overnight. Using Cu pulsed radiation with a wavelength of 0.154 nm, the crystallization of the compound was determined by monitoring the position, shape, and intensity of the reflection from the distribution structure substrate.

2.2.3 Adsorption Properties and Reusability

(1) Establishment of Standard Curve A series of concentration gradient solutions were obtained by step dilution method, and the absorbance of copper ions with different concentrations were measured by flame atomic absorption photometer. This step was repeated for three times to obtain the standard curve.

(2) Influencing Factors of Adsorption Performance A series of $Cu(NO_3)_2$ solutions (250 mL) with different concentrations were prepared. The pH value of the solution was adjusted by 0.1 mg/L NaOH and 0.1 mg/L HCl. Different amount (0.01 g, 0.02 g, 0.04 g, 0.06 g, 0.08 g, 0.10 g) of Isatis Indigotica fort draff was added into the $Cu(NO_3)_2$ solutions with different pH values (1,2,3,4,5,6) and different concentrations of copper ions (20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L, 150 mg/L). The resulting mixtures were oscillated on the oscillator at room temperature for a certain period of time (10 min, 20 min, 30 min, 40 min, 60 min, 75 min, 120 min). 1 mL of supernatant was taken and diluted with pure water in a 50 ml volumetric flask, and then the absorbance of the solution was measured on the flame atomic absorption analyzer after fully oscillating. The concentration value was obtained by automatic conversion of the instrument, and then the original solution concentration value is obtained by multiplying the concentration value by 50. After calculation, the experimental adsorption capacity, adsorption kinetic model parameters, and adsorption isotherm parameters can be obtained.

(3) Reusability After the adsorption process is completed, the adsorbent was separated from the copper ion solution. After being washed, the adsorbent is desorbed with eluent. After desorption, the adsorbent was separated, and the next adsorption-desorption process is cycled for a total of four adsorptions-desorption experiment. Two sets of parallel experiments were carried out to calculate the average value of desorption efficiency.

3 RESULTS AND DISCUSSION

3.1 Characterization of Chemically Modified Isatis Indigotica Fort Draff based Biosorbent

3.1.1 SEM Analysis

The SEM images of RIR, RIR-NaOH, RIR-Na_2CO_3, and RIR-CA are shown in Figure1-(a). The results show that the structure of RIR is relatively dense, and the surface of RIR-NaOH, RIR-Na_2CO_3, and RIR-CA show signs of fiber surface fracture and fiber disintegration, and the surface pores increase. The increase in pores is beneficial to increase the contact area between heavy metal ions and the surface area of cellulose, and to adsorb more heavy metal ions.

3.1.2 FTIR Analysis

The IR spectra of RIR, RIR-NaOH, RIR-Na_2CO_3, and RIR-CA are shown in Figure1-(b). In general, before and after the modification, the peak shape of the IR spectrum is roughly the same, and there is no big shift. Before modification, the peak is broad and strong near 3417 cm-1, indicating that there were many stretching vibration absorption peaks of O-H and N-H on the surface of the Isatis Indigotica fort draff -based biosorbent; the absorption peak of 2927 cm-1 comes from the stretching vibration of saturated C-H bonds, the absorption peak of 1647 cm-1 comes from the stretching vibration of C=O of aliphatic aldehyde, the absorption peak of 1415cm-1 is from the deformation vibration of CH_3- and -CH_2-, the absorption peak of 1153 cm-1 is from the stretching vibration of ester bond, and the absorption peak of 1029cm-1 is from the bending vibration of -OH. After modification, the peak intensity of Isatis Indigotica decreased, the amplitude decreased, and the wave peaks became wider, indicating that the content of various groups on the surface of the modified Isatis Indigotica were reduced (Wei 2003).

3.1.3 TG Analysis

The thermograms of RIR, RIR-NaOH, RIR-Na2CO3, and RIR-CA are shown in Figure1-(c). According to the thermal decomposition of each component of lignocellulosic biomass, Reddy et al. (Xu 2021), Chen et al. (Yang 2016), and Braga et al. (Yang 2020) divided the TG curves of the Lignocellulosic biomass into three stages, namely,

the dehumidification stage, the decomposition of the cellulose molecular skeleton and the loss of hemicellulose, and the decomposition of solid residues. In this experiment, according to the thermogravimetric curve, when the temperature is lower than 120-220 ℃, the weight loss of the sample is between 5% and 8%, mainly due to the evaporation of water in the sample. When the temperature is between 220 and 350 ℃, the curve drops faster, mainly due to the decomposition of cellulose and hemicellulose. The order of the weight loss rate of the four adsorbents is as follows: RIR-NaOH > RIR-Na_2CO_3 > RIR-CA > RIR, which shows that the loss rate of cellulose and hemicellulose of the modified adsorbent is higher. When the temperature is higher than 350 ℃, the weight of the sample changes slowly, which is mainly related to the decomposition of lignin (Yi 2019). In addition, it can also be observed that the thermal stability of the adsorbent after modification is higher than that before modification.

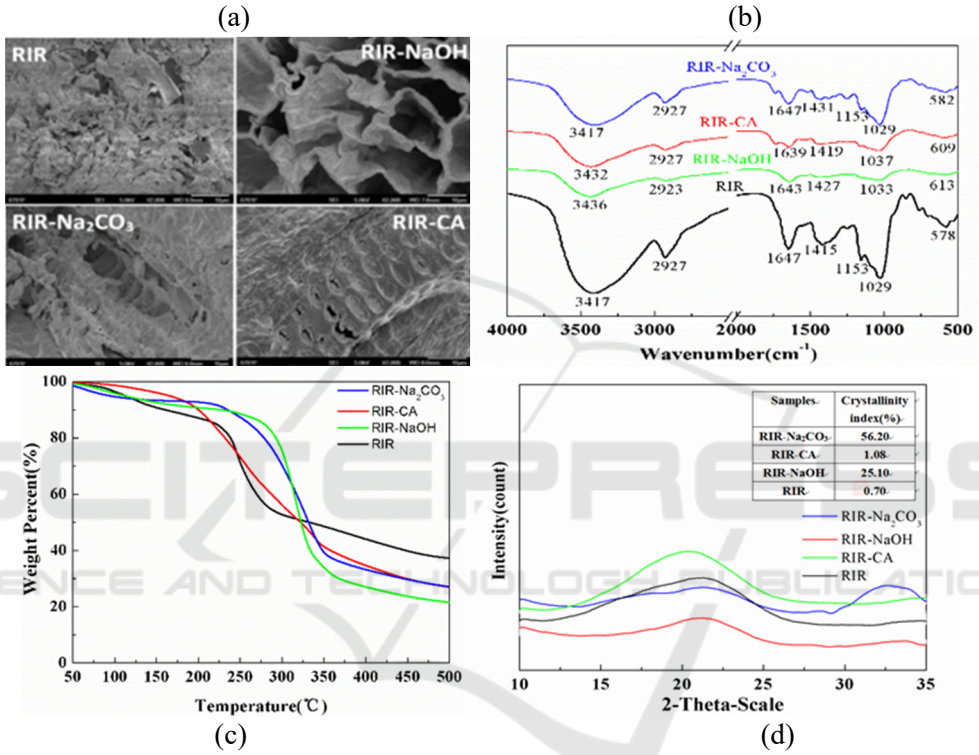

Figure 1: Characterization of RIR, RIR-NaOH, RIR-Na2CO3, and RIR-CA.(a)SEM of RIR, RIR-NaOH, RIR-Na2CO3, and RIR-CA. (b)FTIR spectra of RIR, RIR-NaOH, RIR-Na2CO3 and RIR-CA. (c) TG of RIR, RIR-NaOH, RIR-Na2CO3 and RIR-CA. AR-Na2CO3 and AR-CA. (d)XRD profiles of RIR, RIR-NaOH, RIR-Na2CO3 and RIR-CA.

3.1.4 XRD Analysis

The XRD patterns of RIR, RIR-NaOH, RIR-Na_2CO_3, and RIR-CA are shown in Figure1-(d). The results show that the crystallinity indexes of RIR, RIR-NaOH, RIR-Na_2CO_3, and RIR-CA are 0.7%, 25.10%, 56.20%, and 1.08% respectively. It was found that the crystallinity of the modified adsorbent was higher than that before modification, indicating that the structure of lignin and hemicellulose was destroyed after modification, making the overall structure loose. Secondly, it is found that the crystallinity index of RIR and RIR-CA is very low, which may be due to the changes of Radix Isatidis in the process of chemical treatment since its composition is different from those of the other two Chinese herbal medicines. We need to conduct in-depth research in future.

3.2 Study on the Absorption Behavior of Isatis Indigotica Fort Draff based Biosorbent on Copper ions

3.2.1 The Influence of Solution pH on Adsorption

The effect of solution pH on the adsorption capacity of copper ions is shown in Figure 2-(a). When the

pH is too high, copper ions will exist in the form of precipitation, which is not conducive to adsorption. Therefore, the maximum pH of the solution studied in this experiment is about 6.0. It can be seen from the figure that the adsorption capacity of RIR, RIR-NaOH, RIR-Na_2CO_3, and RIR-CA for copper ions all increases with the increase of pH value. This is mainly due to the high concentration of H+ in the solution at the beginning, which competes with copper ions for the active sites of the adsorbent. Therefore, the adsorption capacity is low. As the pH value increases, the concentration of H+ decreases, which weakens the competition gradually. Therefore, the adsorption capacity is increased. In addition, in the process of pH change, the adsorption capacity of RIR-NaOH and RIR-CA is always higher than that of RIR, and the adsorption capacity of RIR-CA is always higher than RIR-NaOH.

3.2.2 The Effect of Initial Solution Concentration on Adsorption

As shown in Figure 2-(b), the adsorption capacity of RIR, RIR-NaOH, RIR-Na_2CO_3, and RIR-CA for copper ions varies with the adsorption concentration. It can be seen from the figure that with the increase of the initial concentration of the solution, the change trend of adsorption capacity increases first and then remains basically unchanged. The possible reason is that because the dosage of the adsorbent is fixed, the number of adsorption sites is fixed, and the maximum amount of copper ions that can be adsorbed is also fixed. When the concentration of copper ions in the solution is low, the adsorption sites are unsaturated. When the concentration of copper ions in the solution increases to a certain extent, the adsorption sites reach saturation, at which time the adsorption capacity is the largest. Even the concentration of copper ions further increases, the adsorption capacity will no longer change. When RIR, RIR-NaOH, RIR-Na_2CO_3, and RIR-CA reach adsorption equilibrium, their optimal copper ion concentrations in the solution that can be adsorbed are 60, 100, 60, and 60 mg/L, respectively.

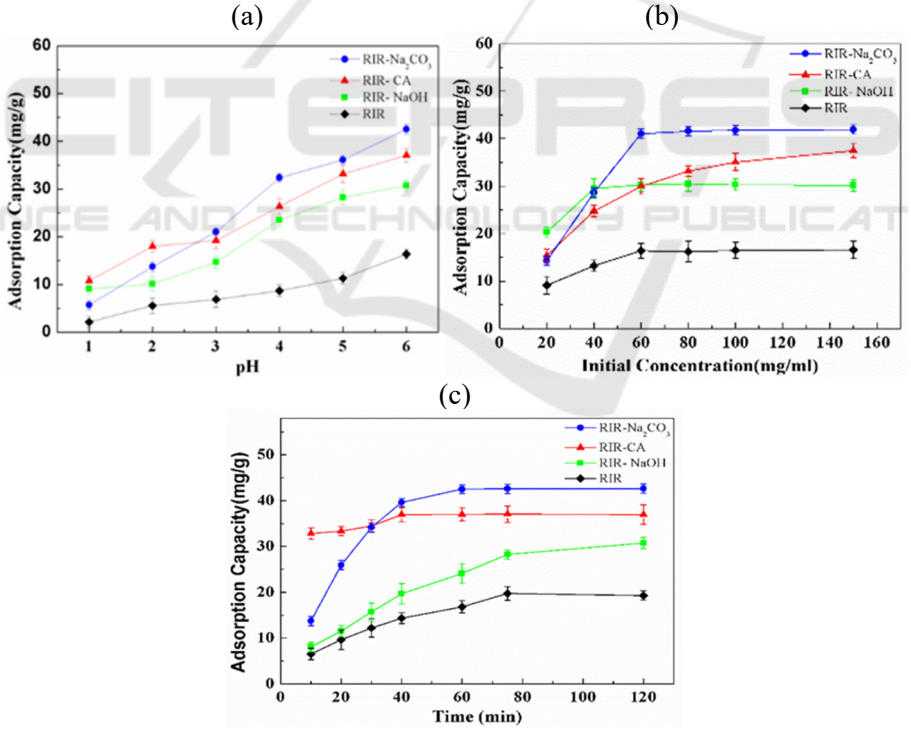

Figure 2: Study on the adsorption effect of Isatis In digotica Fort Draff residue-based bio-adsorbent on Cu2+. (a) Effect of solution pH on the adsorption capacity of Isatis Indigotica Fort Draff based biosorbent.. (b) Effect of initial concentration of solution on the adsorption capacity of Isatis Indig otica Fort Draff based biosorbent. (c) Effect of adsorption time on the adsorption capacity of Isatis Indigotica Fort Draff based biosorbent.

3.2.3 The Effect of Adsorption Time on Adsorption

Figure 2-(c) shows the change of adsorption capacity of copper ions by RIR, RIR-NaOH, RIR-Na2CO3, and RIR-CA with adsorption time. It can be seen from the figure that with the increase of adsorption time, the adsorption capacity increases first and then remains basically unchanged. The possible reason is that at the beginning of the adsorption, there are many sites on the surface of the adsorbent that can be used to adsorb copper ions and there are more free copper ions in the solution. However, as the reaction proceeds, these adsorption sites gradually reach saturation, the copper ion in the solution decreases, the adsorption tends to be balanced, and the adsorption capacity reaches the maximum. In the whole process of adsorption, the adsorption capacity of RIR-NaOH, RIR-Na_2CO_3, and RIR-CA are all higher than that of RIR, and the adsorption capacity follows an order of RIR-Na_2CO_3 > RIR-NaOH > RIR-CA. Therefore, the three modification methods can all increase the adsorption capacity of RIR, and the modification effect of Na_2CO_3 is better than the other two. In addition, in the whole adsorption process, the adsorption time when RIR-CA, RIR-Na2CO3, RIR, and RIR-NaOH reach equilibrium is 40, 60, 75, and 75 min respectively. Therefore, there is no significant change in the adsorption time when RIR-NaOH reaches adsorption equilibrium compared with RIR. The adsorption time of RIR-CA and RIR-Na_2CO_3 is reduced compared with RIR when reaching the adsorption equilibrium, that is, the Na_2CO_3 modification can shorten the adsorption time of the adsorbent.

3.2.4 Adsorption Isotherm

The Langmiur isotherm model and the Freundlich isotherm model were used to fit the adsorption data of the Isatis Indigotica fort draff-based adsorbent, and the formula is as follows:

Langmiur model:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \tag{1}$$

Freundlich model:

$$\log q_e = \log K_F + \frac{1}{n} \times \log C_e \tag{2}$$

It can be seen from Table 1 that the fitting constant obtained by the Langmiur isotherm model is closer to 1, so the Langmiur isotherm model can better describe the adsorption data. It shows that the adsorption of heavy metal ions by the adsorbent is single-layer adsorption, and the adsorption process is chemical adsorption. According to the Langmuir adsorption isotherm, the saturated adsorption capacities of RIR, RIR-NaOH, RIR-Na_2CO_3, and RIR-CA for copper ions are 18.72, 31.91, 54.23, and 47.73 mg/g respectively. It can be seen that the performance of Na_2CO_3 modified Isatis Indigotica fort draff based adsorbent is the best.

Table 1: Adsorption isotherm model and parameters of Isatis Indigotica Fort Draff based biosorbent.

Adsorbent	Langmuir Model			Freundlich Model		
	qmax(mg/g)	K(L/mg)	RL2	KF	n	RF2
RIR	18.72	6.50×10-2	0.987	4.10	3.30	0.769
RIR-NaOH	31.91	1.67×10-1	0.993	4.88	5.47	0.556
RIR-Na_2CO_3	54.23	3.25×10-2	0.919	4.24	1.99	0.742
RIR-CA	47.73	2.63×10-2	0.995	1.91	5.13	0.920

3.2.5 Adsorption Kinetics

The first-order and second-order equations of adsorption kinetics are respectively used to fit the adsorption data of the adsorbent, and the formula is as follows:

The first-order equation of adsorption kinetics:

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

The second-order equation of adsorption kinetics:

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

The results are shown in Table 2. The linear correlation coefficient R_1^2 obtained by quasi first-

order kinetic fitting of the three adsorbents is relatively small, indicating that the reaction does not accord with the relevant characteristics of the quasi first-order reaction. The linear correlation coefficient R_2^2 obtained by the quasi second-order kinetics fitting is greater than that of the quasi first-order kinetics, and the degree of fit is high, indicating that the quasi second-order kinetics model can describe the adsorption data of these three adsorbents well. This also shows that the adsorption process of heavy copper ions on the surface of the Isatis Indigotica fort draff based biosorbent is chemical adsorption.

Table 2: Adsorption kinetic model and parameters of Isatis Indigotica Fort Draff based biosorbent.

Adsorbent	qe,exp (mg/g)	Quasi first order dynamics model			Quasi second order dynamics model		
		qe,cal(mg/g)	k1(min−1)	R_1^2	qe,cal(mg/g)	k_2(g/mg·min-1)	R_2^2
RIR	16.54	14.85	3.71×10-2	0.566	20.56	1.71×10-3	0.982
RIR-NaOH	31.00	49.18	4.05×10-2	0.527	44.68	4.36×10-4	0.992
RIR-Na_2CO_3	42.65	42.67	7.03×10-2	0.862	51.15	1.09×10-3	0.971
RIR-CA	37.55	3.85	2.14×10-2	0.564	37.69	1.47×10-2	0.991

3.2.6 Reusability

LR-Na_2CO_3, the best bio-adsorbent for Cu^{2+}in our experiment, was selected to study the adsorption and desorption conditions. The regeneration and reusability of LR-Na_2CO_3 for heavy metals Cu^{2+} were evaluated by four consecutive adsorption–desorption cycles (Figure 3). It showed that LR-Na_2CO_3 has good reusability for Cu^{2+}, the adsorbability remained higher than 74% after four consecutive adsorption–desorption cycles, consistent with other reports, which indicated that the LR-Na_2CO_3 is a suitable potential adsorbent for the removal of the heavy metal ions Cu^{2+} from water.

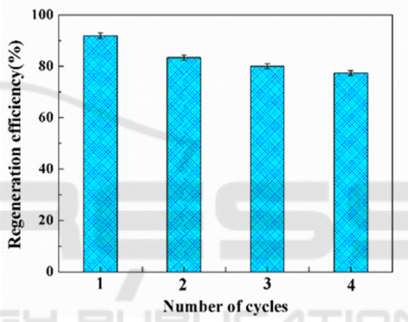

Figure 3: Reusability of RIR-Na_2CO_3.

3.3 Comparison with Other Adsorbents

The qmax value obtained in this study was compared with various biosorbents reported in the literature for removing $^{Cu2+}$, as shown in Table3. The results show that the adsorption capacity of RIR-CA and RIR-Na2CO_3 are higher than that of other biosorbents (such as activated carbon fiber, modified sawdust cellulose, and so on).

Table 3: Comparison of Isatis Indigotica Fort Draff and other adsorbents.

Absorbent	Metal Ion	qmax(mg/g)	Reference
RIR-CA		47.73	this study
RIR-Na_2CO_3		54.23	this study
Autotrophic nitrifying granular sludge		15.02	Zhang et al. (Yu 2019)
Activated carbon fiber	Cu^{2+}	25.51	Yu J, Chi C, Zhu B, Qiao K, Yan S.(Yuan 2019)
Modified sawdust cellulose		4.33	Ulfa S M, Chamidah N, Kurniawan A.(Zhang 2020)
Papermaking sludge		28.788	Dai C, Zhang Y. (Zhang 2020)

4 SUMMARY

The Isatis Indigotica fort draff was used as raw materials and modified with NaOH, Na_2CO_3, and citric acid to prepare the Isatis Indigotica fort draff based biosorbent, which was used in the study of the adsorption of heavy metal copper in water. The structure of the modified biosorbent was characterized by FTIR, SEM, TG and XRD. It was found that the structure of the modified biosorbent was loose and the cellulose surface active groups increased. The adsorption performance of RIR, RIR-NaOH, RIR-Na_2CO_3, and RIR-CA is better than that of RIR. The order of the maximum adsorption capacity of the modified Isatis Indigotica fort draff based adsorbent for copper ions is: RIR-Na_2CO_3 > RIR-NaOH > RIR-CA > RIR. The adsorption process of copper ion conforms to the quasi first-order kinetic model and Langmuir model, that is, the adsorption of copper ion on its surface is chemical adsorption. The adsorption capacity of Na_2CO_3 modified Radix Isatidis for copper ions is the best, and the maximum adsorption capacity after four consecutive adsorption-desorption cycles is about 77% of that at the first adsorption. In conclusion, the modification of NaOH, Na_2CO_3, and citric acid can not only improve the adsorption performance of Isatis Indigotica fort draff, but also reduce the environmental pollution caused by the unreasonable use of Isatis Indigotica fort draff and improve the resource utilization rate of Isatis Indigotica fort draff.

ACKNOWLEDGEMENT

This work was supported by NSFC (82160900), Innovation Fund Project of Higher Education in Gansu Province (2021B-159), Open Foundation of Collaborative Innovation Center for Prevention and Control by Chinese Medicine on Disease Related Northwestern Environment and Nutrition (998/99860202) , Open Foundation of Traditional Chinese Medicine Research Center of Gansu Province (ZYZX-2020-ZX16) and Research on prevention and control of COVID-19 by integrated Traditional Chinese and Western Medicine(2020C-36).

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