Preparation of Chemically Modified Residue-based Bio-adsorbents in Astragalus and Study on Its Adsorption Performance

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Abstract: [Objective] Astragalus residues were prepared with NaOH, Na_2CO_3 and citric acid modification, and their adsorption capacity for Cu^{2+} was studied for the removal of metal ions from simulated wastewater. [Method] Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), thermogravimetry (TG) and X-ray diffraction (XRD) were adopted to characterize the morphology and surface structure of bio-adsorbents; through static adsorption experiments, the effects of adsorbent dosage, pH, adsorption time and initial concentration of Cu^{2+} solution on the adsorption performance of the adsorbent were investigated; the desorption performance of the adsorbent was studied by dynamic experiments, the adsorption principle of the adsorbent was clarified, and a certain theoretical basis was provided for the reuse of Astragalus residues. [Result] The modification of NaOH, Na_2CO_3 and citric acid can improve the adsorption capacity of Astragalus residues to Cu^{2+} in water body, thereby reducing its pollution to the environment and realizing the resource utilization of Astragalus residues. [Conclusion] Astragalus can be used as a raw material for the preparation of adsorbents for removing heavy metal pollutants in water, and the modified adsorbent has excellent performance.

1 INTRODUCTION

With the rapid economic development and the continuous progress of society, the living standards of people have gradually improved. At the same time, the amount of wastewater discharged has increased year by year, causing serious pollution to the environment. Cu^{2+} is one of the most common heavy metal ions in wastewater. As one of the essential trace elements of human body and animals and plants, a minute amount of Cu^{2+} can promote the growth of animals and plants and normal life activities of human body. However, long-term accumulation of Cu^{2+} will cause physiological obstruction of animals and plants, development stagnation, and even will result in a large number of deaths, so that the whole aquatic ecosystem will disorder or even will collapse. Through the enrichment of the food chain, the human body ingests a large number of contaminated animals and plants, causing toxicity accumulates and damage to the human body, such as Wilson's disease (WD), which is a chromosomal recessive disease, dominated by adolescents and is a congenital copper metabolic disorder. CuEXC is considered to be a specific marker of copper overload in WD (Estela 2021). Excessive copper content in adults can lead to many undesirable consequences such as high blood pressure, coronary heart disease, arteriosclerosis, and even endanger human health (Wang 2015).

In recent years, China and most other countries have realized the hazards of wastewater pollution and the urgency of water shortages, and have begun to take various measures to re-treat wastewater for cyclic utilization and reducing environmental hazards, such as electric flocculation method (Bian 2021), microbiological method (Zhang 2021), electrodeposition method (Chen 2021), biochar adsorption method (Das 2021), etc. Compared with other methods, the adsorption method has the advantages of a wide application range, no secondary pollution, high treatment efficiency, low operating cost, and relatively simple operation (Shao

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2019, Lan 2020). Therefore, the adsorption method is currently the most promising method. In recent years, researches on adsorbents have emerged one after another. Among them, traditional Chinese medicine residue contains a large amount of lignin and cellulose, which can effectively adsorb heavy metals and is one of the emerging mainstreams in the preparation of adsorbents.

Astragalus is a legume plant often used as a traditional medicine in China, Japan, Korea and Southeast Asia (Wang 2018, Zhu 2020). *Astragalus* has anti-tumor effect and can enhance resistance (Wu 2001, Meng 2016, Deng 2018, Yu 2019, Huang 2019, Ma 2020, Zhu 2020). A variety of active substances can be extracted by processing *Astragalus*, such as flavonoids, saponins, polysaccharides and amino acids (Zheng 2019, Li 2019, Zheng 2019, Chu 2019). In recent years, with the gradual improvement of *Astragalus* processing industry technology, the output of *Astragalus* residues has also increased. If these drug residues are not treated in time, they will cause serious pollution to the environment.

Studies have shown that *Astragalus* residues are rich in lignocellulose and other substances (Wang 2019). Lignocellulose is combined by cellulose, hemicellulose and lignin through non-covalent force and covalent cross-linking (Yang 2018). Because the surface of lignin, cellulose and hemicellulose contains many active functional groups such as carbonyl groups and hydroxyl groups, they can be combined with heavy metal ions in various ways such as surface precipitation (Wang 2020, Qiu 2020, Tan 2020) to remove heavy metals in the water environment. Feng (Feng 2017) used the waste residue of *Astragalus* to prepare a bio-adsorbent, which can adsorb Pb^{2+} well. However, the cellulose surface functional groups in *Astragalus* residues are often encapsulated in it, which affects the adsorption performance of *Astragalus* residues on heavy metal ions. Therefore, chemical modification is necessary to increase the adsorption performance of *Astragalus* residues.

In this study, NaOH, Na_2CO_3 and citric acid were used to modify the *Astragalus* residues, and the *Astragalus* residue-based bio-adsorbent was prepared for the adsorption of heavy metal Cu^{2+} in the aqueous solution. The samples were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), thermogravimetry (TG) and X-ray diffraction (XRD). Through static adsorption experiments, the effects of adsorbent dosage, solution pH, adsorption time and initial Cu^{2+} concentration on the adsorption performance of the adsorbent were investigated; the desorption performance of the adsorbent was studied through dynamic experiments, and the adsorption mechanism of the adsorbent was clarified, which can provide a theoretical basis for the reuse of *Astragalus* residues.

2 MATERIALS AND EXPERIMENTS

2.1 Materials

The *Astragalus* residues used in the experiment came from Huirentang Pharmacy (Lanzhou, China), and were repeatedly washed to remove residual organic components. Water used in the experiment was deionized water.

2.2 Experiments

2.2.1 Adsorbent Preparation

(1) Decolorization treatment: *Astragalus* was bought from a pharmacy, and washed with deionized water for 1-2 times, changing the water and boiling for 3 times (30 min/time), and drying at 65°C, crush, then passing through a 40-mesh sieve. The prepared drug residue and methanol were mixed and stirred at a solid-liquid ratio of 1:5, and stirred until the pigment and biologically active ingredients in the drug residue were completely removed. The drug residue was washed with distilled water and dried at 65°C. The prepared pre-treatment drug residue is referred to as *Astragalus* residues for short, denoted as AR.

(2) Modification:

①NaOH modification: Weigh a certain amount of AR, add 1 mol/L NaOH, mix in a solid-to-liquid ratio of 10:1, stir magnetically for 4 h (120 r/min), shake the residue with deionized water and wash it to neutrality, filter the medicine residue with a sand filter, dry it, and name it as NaOH modified *Astragalus* residues, denoted as AR-NaOH.

②Na_2CO_3 modification: Weigh a certain amount of AR, add 1 mol/L Na_2CO_3, mix at a solid-liquid ratio of 10:1, and magnetically stir for 4 h (120 r/min). Then it was washed with deionized water to neutrality, filtered with a sand filter, dried, and named as Na_2CO_3 modified *Astragalus* residues, denoted as: AR-Na_2CO_3.

③ Citric acid modification: AR was firstly pre-treated with 0.1 mol/L NaOH for 30 min, then mixing 0.6 mol/L citric acid solution with the pre-treated dregs at a ratio of 10:1 for modification, and magnetic stirring for 4h (120 r/min). Finally, the drug residue was washed with deionized water, washed to neutrality, dried, and named as citric acid modified *Astragalus* residues, denoted as AR-CA. All *Astragalus* residue-based bio-adsorbents were collectively named AR-Ts.

2.2.2 AR-Ts Structure Characterization

(1) FTIR: Fourier infrared spectrometer (FTIR, Nicolet Nexus, USA) was used to study the structure and chemical bonds of its molecules. The samples for analysis were dried before use, ground in a mortar, mixed with potassium bromide powder and then pressed into a transparent sheet. The experiment was carried out in the spectral range (4000-400cm^{-1}).

(2) SEM: Scanning electron microscopy (SEM; JSM-6701F, JEOL, Japan) was used to study the morphology of lignocellulosic compounds. The samples for analysis were stored in an oven at a temperature of 50°C overnight.

(3) TG: Perkin Elmer TGA-7 thermogravimetric analyzer (Perkin-Elmer Cetus Instruments, Norwalk, CT) was used to study the thermal stability and composition of the adsorbents. About 10 mg of the sample was weighed in a crucible and placed in a sample holder. The sample was heated from room temperature to 800°C (heating rate 10°C/min), the purge gas was nitrogen, and the flow rate was 20 ml/min.

(4) XRD: X-ray diffractometer (JEOL, JDX-3530, 2 kW, Tokyo, Japan) was used to study the crystalline properties of the cellulose component. Before analysis, the sample was ground into a finer and uniform particle size powder, stored in an oven at 50°C overnight, using CuK pulsed radiation with a wavelength of 0.154 nm, and determining the crystallinity degree of the compound by monitoring the position, shape and intensity of the reflection from the distribution structure substrate.

2.2.3 Adsorption Performance

First, a set of $Cu(NO_3)_2$ solutions was prepared with a concentration gradient, and a Cu^{2+} standard curve was established by flame atomic absorption spectrophotometry. Then, a certain concentration of $Cu(NO_3)_2$ solution was prepared to adjust the pH of the solution. A certain quality of *Astragalus* residue-based adsorbent was placed in a conical flask with a certain pH and a certain concentration of $Cu(NO_3)_2$ solution, and oscillated on a constant temperature oscillator for a certain period of time. The adsorption capacity, adsorption kinetic model parameters and adsorption isotherm parameters of the adsorbent can be obtained by measurement and calculation.

3 RESULTS AND ANALYSIS

3.1 Characterization of Chemically Modified Astragalus Residue-based Bio-adsorbent

3.1.1 SEM Analysis

The scanning electron micrographs of AR, AR-NaOH, AR-Na_2CO_3 and AR-CA are shown in Figure 1(a). It can be seen from the figure that the structure of AR is relatively dense, and the surface of AR-NaOH, AR-Na_2CO_3 and AR-CA has more pores and loose structure, which may be caused by the erosion and fragmentation of lignocellulose. The results show that the modifiers have a certain effect on the AR surface, and the modified *Astragalus* residue adsorbent is easier to adsorb Cu^{2+} in water.

3.1.2 FTIR Analysis

Figure 1(b) is the infrared spectrum of AR, AR-NaOH, AR-Na_2CO_3 and AR-CA. It can be seen from the figure that the absorption peak of AR: the peak at 3411 cm^{-1} is stronger, indicating that the surface of residue-based bio-adsorbent in *Astragalus* is rich in O-H; the peak at 2927 cm^{-1} is the stretching vibration of the C-H bond in methyl and methylene; the peak at 1739 cm^{-1} is the C=O stretching vibration in the acid ester; the peak at 1639 cm^{-1} is the C=O stretching vibration in the protein, and the peak at 1373 cm^{-1} is the CO stretching vibration of the phenyl-hydroxyl group in lignin, the peak at 1249cm^{-1} is the C-O-C stretching vibration of lignin, the peak at 1157 cm^{-1} is the C-O-C stretching vibration of the cellulose ester group. The peak at 1030cm^{-1} is the bending vibration of –OH (Li 2019).

In AR-NaOH, the peak at 1739 cm^{-1} disappeared, indicating that NaOH can cleave the ether ester bond, and the ether ester bond in lignocellulose is the main chemical bond connecting lignin and hemicellulose. Comparing the peaks before and after the modification, the peak intensity of some groups of the Astragalus residue adsorbent after the modification decreased, and the amplitude decreased, indicating that the content of chemical groups in the Astragalus residue adsorbent decreased after the modification.

3.1.3 TG Analysis

Figure 1(c) is the thermogravimetric diagram of AR, AR-NaOH, AR-Na_2CO_3 and AR-CA. The thermal degradation of cellulose can be divided into three stages: (1) AR, AR-NaOH, AR-Na_2CO_3 and AR-CA began to decrease slowly at 40-240℃, mainly due to the evaporation of water in the sample and the loss of hemicellulose; (2) The rapid weight loss of AR-NaOH, AR-Na_2CO_3 and AR-CA at 240-330℃, and AR at 240-380℃ may be due to the decomposition of the cellulose molecular skeleton and the degradation of hemicellulose. The weight loss rate of AR-NaOH, AR-Na_2CO_3 and AR-CA is smaller than AR, indicating that the cellulose and hemicellulose content in AR-NaOH, AR-Na_2CO_3 and AR-CA is lower than AR; (3) In the final stage, the solid residue continues to decompose at a very slow rate. In addition, it can also be found that the thermal stability of the adsorbent after modification is lower than that before modification.

3.1.4 XRD Analysis

Figures 1(d) are XRD patterns of AR, AR-NaOH, AR-Na_2CO_3 and AR-CA. Studies have shown that different treatment methods break the hydrogen bonds between and within the fiber chains of lignocellulose, resulting in different changes in the cellulose crystal structure. In the adsorbent, lignocellulose is mainly used for adsorption, and lignocellulose usually exists in the form of amorphous and crystalline states. Among them, cellulose is mainly present in a crystalline state. Therefore, the crystallinity increases when lignin and hemicellulose are destroyed to a certain extent. The results showed that compared with the unmodified sample (crystallinity index 76.12%), the crystallinity index after citric acid treatment, Na_2CO_3 treatment and NaOH treatment increased to 80.87%, 77.88% and 78.82%, respectively, which means that the adsorption capacity of the three *Astragalus* residue-based adsorbents after modification is essentially the same.

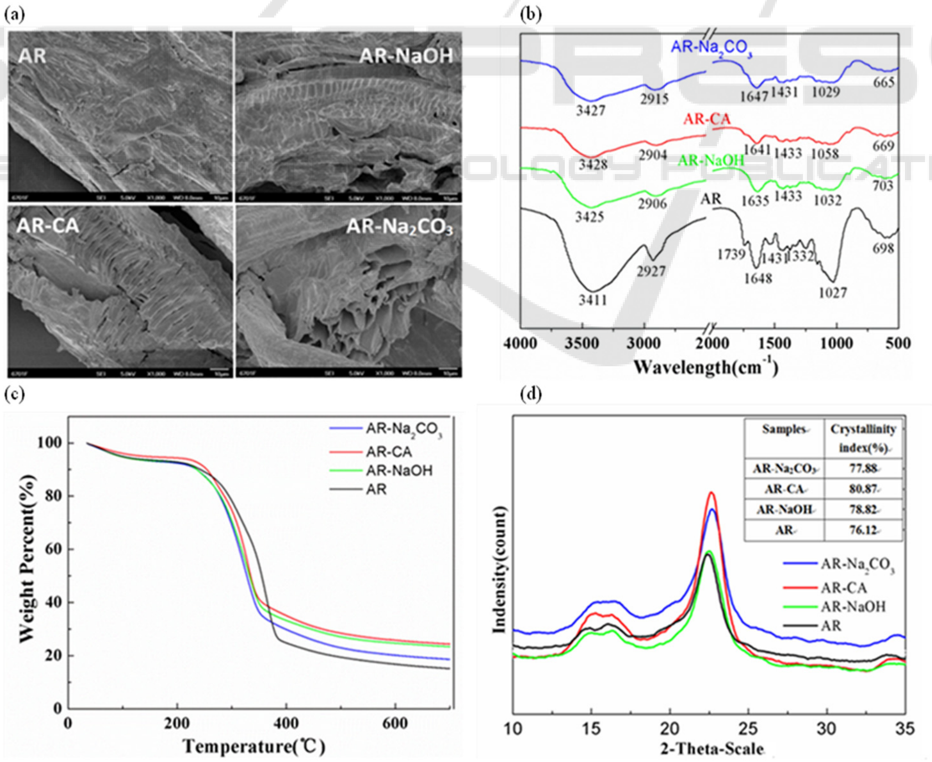

Figure 1: Characterization of AR, AR-NaOH, AR-Na2CO3 and AR-CA. (a) Electron micrographs of AR, AR-NaOH, AR-Na2CO3 and AR-CA. (b) Infrared spectra of AR, AR-NaOH, AR-Na2CO3 and AR-CA. (c) TG results of AR, AR-NaOH, AR-Na2CO3 and AR-CA. (d) XRD results of AR, AR-NaOH, AR-Na2CO3 and AR-CA.

3.2 Study on the Adsorption Behavior of Astragalus Residue-based Bio-adsorbent on Cu^{2+}

3.2.1 Effect of Solution pH on Adsorption

Figure 2 shows the effect of solution pH on Cu^{2+} adsorption capacity. It can be seen from the figure that, firstly, as the pH of the solution increases, the adsorption capacity of the four adsorbents for Cu^{2+} tends to increase, which can be related to the high concentration of H^+ inhibiting the reaction and the low concentration of H^+ promoting the reaction. When the solution pH=6, the adsorption capacity of the four adsorbents is the largest. The maximum adsorption capacities of AR, AR-NaOH, AR-Na_2CO_3 and AR-CA are 19.7 mg/g, 31.05 mg/g, 30.53 mg/g and 30.55 mg/g, respectively. In addition, in the whole adsorption process, the adsorption capacity of AR-NaOH and AR-CA are both higher than AR, and when the solution pH=1 and pH=6, the maximum adsorption capacity of AR-NaOH is slightly higher than AR-CA. When the pH=2~5, the maximum adsorption capacity of AR-CA is higher than that of AR-NaOH.

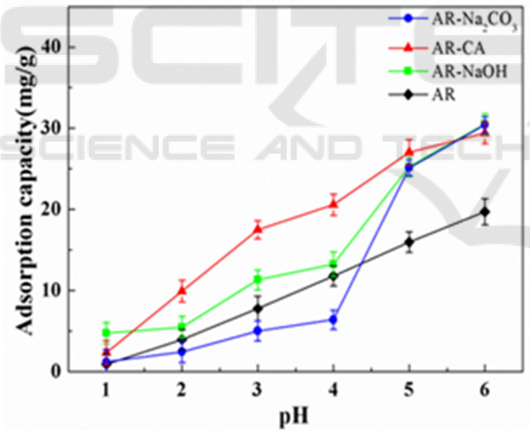

Figure 2: The effect of solution pH on the adsorption capacity of residue-based bio-adsorbent in Astragalus.

3.2.2 Effect of Initial Concentration of the Solution on Adsorption

Figure 3 shows the results of the adsorption capacity of AR, AR-NaOH, AR-Na_2CO_3 and AR-CA on Cu^{2+} with the different initial Cu^{2+} concentrations. It can be seen from the figure that, first of all, with the increase of the initial concentration of the Cu^{2+}, the adsorption capacity of the four adsorbents all shows a trend of increasing first and then unchanged or slightly decreasing, which may be mainly related to the change of the Cu^{2+} concentration in the solution during the adsorption process and the fixed number of adsorption sites, and the optimal initial Cu^{2+} concentrations of the solution that can be adsorbed by AR, AR-NaOH, AR-Na_2CO_3 and AR-CA are 80 mg/L, 100 mg/L, 100 mg/L and 80 mg/L, respectively. Secondly, as the initial Cu^{2+} concentration increases, the adsorption capacities of AR-NaOH, AR-Na_2CO_3 and AR-CA are all higher than AR, and the adsorption capacities of AR-NaOH, AR-Na_2CO_3 and AR-CA at equilibrium are essentially the same.

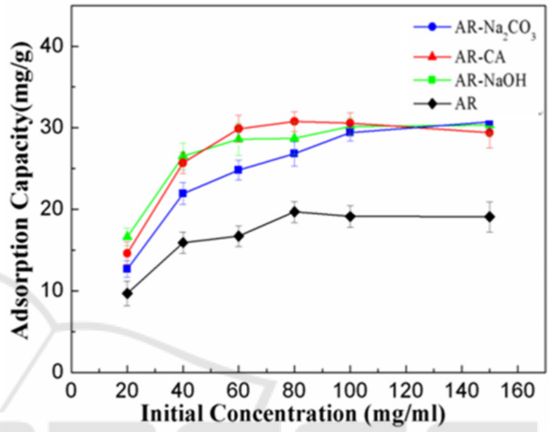

Figure 3: The effect of initial solution concentration on the adsorption capacity of residue-based bio-adsorbent in Astragalus.

3.2.3 Effect of Adsorption Time on Adsorption

Figure 4 shows the results of the adsorption capacity of AR, AR-NaOH, AR-Na_2CO_3 and AR-CA for Cu^{2+} with the change of adsorption time. It can be seen from the figure that, first of all, as the adsorption process progresses, the adsorption capacity of the four adsorbents for Cu^{2+} all presents a trend of rapid increase and then equilibrium, which maybe related to the emptier adsorption sites on the surface of the adsorbent at the beginning of adsorption. In the reaction progresses, the adsorption capacity increases rapidly. When the adsorption sites reach saturation, the adsorption capacity no longer changes. In the whole adsorption process, the adsorption capacities of AR-NaOH, AR-Na_2CO_3 and AR-CA are all higher than AR, and the adsorption capacities of AR-NaOH, AR-Na_2CO_3 and AR-CA are basically the same when the adsorption equilibrium is reached. The effects of these modifiers on the modification of Astragalus are basically the same. Secondly, the time for AR, AR-NaOH, AR-Na_2CO_3 and AR-CA to reach adsorption equilibrium is 80min, 30min, 30min and 20min, respectively, that is, the two modification methods shorten the adsorption time when the adsorption equilibrium is reached to varying degrees.

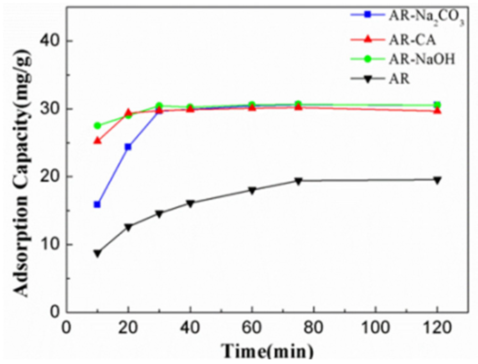

Figure 4: The effect of adsorption time on the adsorption capacity of residue-based bio-adsorbent in Astragalus.

3.2.4 Adsorption Isotherm

The Langmuir model (1) and Freundlich model (2) were used to fit the adsorption data of the residue-based adsorbent for *Astragalus*, and the formulae are as follows:

Langmuir model:

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

Freundlich model:

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

Table 1: Astragalus drug residue-based bio-adsorbent adsorption isotherm models and parameters.

Adsorbent	Langmuir model			Freundlich model		
	q_{max}(mg/g)	K(L/mg)	R_L^2	K_F	n	R_F^2
AR	22.15	5.42×10^{-2}	0.980	2.18	2.96	0.768
AR-NaOH	33.91	6.85×10^{-2}	0.990	1.93	3.50	0.731
AR-Na_2CO_3	38.65	2.87×10^{-2}	0.990	1.07	2.30	0.883
AR-CA	33.85	6.78×10^{-2}	0.965	2.22	2.89	0.654

It can be seen from Table 1 that, compared with the Freundlich model, the Langmuir model has a larger correlation coefficient, which shows that the quasi-Langmuir model can better fit the adsorption process of Cu^{2+} by the residue-based adsorbent for Astragalus, that is, the adsorption of the four residue-based adsorbents to heavy metal ions Cu^{2+} is dominated by single-layer adsorption. According to Langmuir adsorption isotherm, the saturated adsorption capacities of AR, AR-NaOH, AR-Na_2CO_3 and AR-CA for Cu^{2+} are 22.15 mg/g, 33.91 mg/g, 38.65 mg/g and 33.85 mg/g, respectively. It can be seen that the three modified methods of adsorbents have comparable adsorption effects on Cu^{2+} in water.

3.2.5 Adsorption Kinetics

The first-order adsorption kinetics (3) and second-order adsorption kinetics (4) equations were used to fit the adsorption data of the adsorbent, and the formulae are as follows:

First-order adsorption kinetics:

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

Second-order adsorption kinetics:

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

It can be seen from Table 2 that, compared with the quasi-first-order kinetic model, the correlation coefficient of the quasi-second-order kinetic model is larger, above 0.990. It shows that the quasi-second-order kinetic model can better fit the adsorption process of Cu^{2+} by the adsorbent, that is, the adsorptions of Cu^{2+} by the three residue-based adsorbents for *Astragalus* are mainly chemical adsorption.

3.2.6 Reusability of Adsorbent

AR-Na_2CO_3 is the best bio-adsorbent for studying adsorption and desorption conditions in this experiment. Through four consecutive cycles of adsorption and desorption, the regeneration and repeatability of AR-NaOH on heavy metal Cu^{2+} were evaluated. As shown in Figure 3, the results show that AR-Na_2CO_3 has good reusability. After four consecutive adsorption-desorption cycles, the adsorption rate is still higher than 70%, which is consistent with other reports (Chct 2020, Shi 2020, Mok 2020, Maaloul 2021, Pavithra 2021). The report shows that AR-Na_2CO_3 is a suitable potential adsorbent for removing heavy metal ions Cu^{2+} in water.

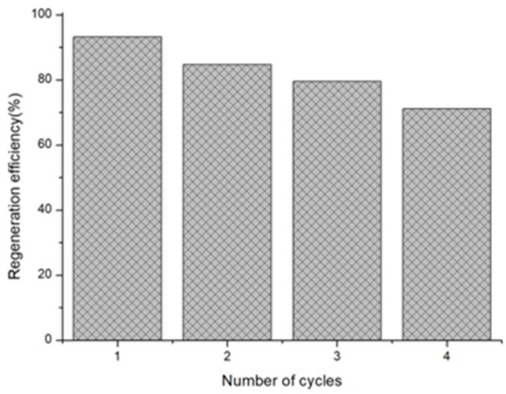

Figure 5: Reusability of AR-Na_2CO_3.

3.3 Comparison with Other Adsorbents

The q_{max} value obtained in this study was compared with various celluloses reported in the literature for removing Cu^{2+} as bio-adsorbents, as shown in Table 3. The results showed that, except that the adsorption capacity of saponified polygonum cuspidatum fiber is slightly higher than AR-NaOH, the adsorption capacity of AR-NaOH and AR-Na_2CO_3 are higher than other bio-adsorbents (such as activated carbon fiber and coffee grounds).

4 CONCLUSIONS

Table 2: Adsorption kinetic model and parameters of residue-based bio-adsorbent for *Astragalus*.

Adsorbent	$q_{e, exp}$(mg/g)	Quasi-first-order kinetic model			Quasi-second-order kinetic model		
		$q_{e, cal}$(mg/g)	k_1(min^{-1})	R_1^2	$q_{e, cal}$(mg/g)	k_2(g/mg·min^{-1})	R_2^2
AR	19.70	20.23	4.16×10^{-2}	0.931	22.31	3.01×10^{-3}	0.997
AR-NaOH	31.05	1.94	1.59×10^{-2}	0.443	30.86	3.69×10^{-3}	0.999
AR-Na_2CO_3	30.72	6.88	3.94×10^{-2}	0.657	32.65	5.13×10^{-3}	0.994
AR-CA	30.55	1.67	1.21×10^{-2}	0.127	30.06	5.69×10^{-2}	0.997

Table 3: Comparison of Cu^{2+} adsorption capacity of various bio-adsorbents.

Bio-adsorbent	Metal ion	q_{max}（mg/g）	References
AR-NaOH		33.91	This research
AR-Na_2CO_3		38.65	This research
Activated carbon fiber		25.51	Yu 2019
Waste coffee grounds	Cu^{2+}	13.33	Sadok 2019
Papermaking sludge		28.788	Dai 2019
Modified sawdust cellulose		4.33	Ulfa 2019
Saponified polygonum cuspidatum residue		34.482	Liu 2017

Using *Astragalus* as raw material, three kinds of residue-based bio-adsorbents for *Astragalus* modified by NaOH, Na_2CO_3 and citric acid were successfully prepared. By using the prepared adsorbent to adsorb Cu^{2+} in water, the adsorption performance of Cu^{2+} in water was studied. Their structures were characterized by FTIR, SEM, TG and XRD, and it was found that the structures of the modified bio-adsorbents are looser than before. The crystallinities of the three adsorbents after modification are basically the same, indicating that the contents of crystalline cellulose of the three adsorbents after modification are basically the same, that is, the adsorption performances are also basically the same. The results show that the adsorption performances of AR-NaOH, AR-Na_2CO_3 and AR-CA are better than AR, the adsorption capacities of AR-NaOH, AR-Na_2CO_3 and AR-CA to Cu^{2+} are equivalent, and the maximum adsorption capacities are about 30 mg/g; The adsorption equilibrium time of AR-NaOH (30 min), AR-Na_2CO_3 (30 min) and AR-CA (20 min) is shorter than AR (80 min). The adsorption processes of these adsorbents to Cu^{2+} accord with the quasi-first-order kinetic model and Langmuir model. In summary, the modification of NaOH, Na_2CO_3 and citric acid can not only improve the adsorption capacity of *Astragalus* residues on Cu^{2+} in water, but also reduce the environmental pollution caused by *Astragalus* residues and realize the resource utilization of it.

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