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Kinetic and thermodynamic studies of the biosorption of Ni(Ⅱ) by modified rape straw

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Abstract

Biosorption equilibrium, kinetics and thermodynamics of Ni(Ⅱ) onto the modified rape straw (MRS) by $ZnCl_2$ were studied in a batch system with respect to pH, temperature and initial metal ion concentration. The Ni(Ⅱ) removal rate increased with rising pH values, reaching about 99.7% at pH 6.5. The biosorption efficiency of Ni(Ⅱ) to the biomass decreased as the initial concentration of metal ions was increased. But it is less likely to be affected by temperature from 303K to 323K. The adsorption data fit Langmuir adsorption isotherm at 303K and 313K. According to Langmuir isotherm, the theoretical maximum adsorption capacity of MRS was 9.17mg·g^{-1} and 10.45mg·g^{-1} at 303K, 313K, respectively. The pseudo-first-order and pseudo-second-order kinetic models were applied to test the experimental data for initial Ni(Ⅱ). The pseudo-second-order kinetic model provided the best correlation of the used experimental data. Thermodynamic parameters can be calculated by Gibbs equation, ΔG is negative, but ΔH is positive, it can be concluded that the process of removing Ni(Ⅱ) by MRS are spontaneous and endothermic. The XPS spectrum of nickel-treated biosorbent reveals that Ni(Ⅱ) is really sorbed onto biosorbent.

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Keywords: adsorption; nickel ions; isotherms; kinetics; thermodynamics

1. Introduction

Heavy metals[1] have great harm to environment. Such as excessive nickel ions can cause inflammation and psychasthenia to people[2]. In the treatment of wastewater polluted by heavy metals, conventional methods usually have characteristics of high cost, low efficiency, secondary pollution etc. Therefore, looking for an economic and

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effective method to remove heavy metals has important meanings. A large amount of agricultural wastes were produced every year in China, but most of them are not used effectively. The main components of rape straw(RS) are cellulose, hemicellulose and lignin. This makes the rape straw has functional groups like hydroxyl and carboxyl, making RS has ability of adsorbing metal ions. Studies indicate that agricultural waste such as rice husk[3], Sunflower stalk[4], juice industrial waste[5], etc can adsorb heavy metal ions. But the study of the adsorption of Ni(Ⅱ) by modified rape straw (MRS) has not been reported. In this paper, removal efficiency and adsorption solutions of Ni(Ⅱ) by MRS are mainly investigated, which provides basic technical parameters for its practical application.

2. Materials and methods

2.1. Preparation of Surface Modified rape straw

Rape straw (RS) was collected at the local farm and then was washed with distilled water. Subsequently, RS was dried for 2 hours at 100℃.Then the dried RS was passed through different sieve size. The chemical modification of RS by $ZnCl_2$ was made according to the similar method previously described by Yu Chen[6]. The surface modified Rape straw were abbreviated as MRS and used as an adsorbent for the removal of nickel ions from the aqueous solution. The surface morphology of the adsorbent was analyzed using XL30-esem(FEI Company, USA).

2.2. Ni(Ⅱ) solutions for absorption experiments

Ni(Ⅱ) solutions were obtained by diluting $1g{\cdot}L^{-1}$ of stock Ni(Ⅱ) solution, which had been got by dissolving a weighed quantity of $Ni(NO_3)_2{\cdot}6H_2O$. Analytical grade reagents were used in all cases.

2.3. Experiment method

Batch Ni(Ⅱ) adsorption studies were performed by mixing requisite quantity of MRS with 80 mL of solution of varying Ni(Ⅱ) concentrations. Initial pH was adjusted using $0.1mol{\cdot}L^{-1}$HCl or $0.1mol{\cdot}L^{-1}$NaOH. The adsorption of Ni(Ⅱ) was carried out in a shaker at room temperature. The solution was intermittently sampled and centrifuged at 6000rpm for 5min. The supernatant was analyzed for Ni(Ⅱ) concentration by eriochrome black T (EBT) spectrophotometric method [7](UV-754, Shanghai, China).

The adsorption capacity for Ni(II) ions adsorbed per gram of adsorbent(q, $mg{\cdot}g^{-1}$) and Ni(Ⅱ) removal rate (R%) were calculated according to the following equation.

$$q = \frac{(C_0 - C_t)V}{w} \qquad R = \frac{C_0 - C_t}{C_0} \times 100\%$$

where C_0 is the initial Ni(Ⅱ) concentration ($mg{\cdot}L^{-1}$); C_t is concentration at time t; w is dry weight of MRS. V is the volume of the Ni(II) solution (L).

3. Results and discussion

3.1. Characterization of the RS and MRS

The adsorption capacity of the adsorbent mainly depends upon the porosity and also the chemical reactivity. Fig. 1(a), 1(b) and 1(c) show the SEM images of RS, MRS and MRS adsorption, respectively.

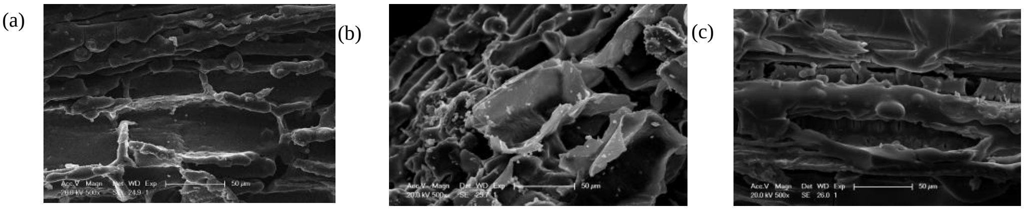


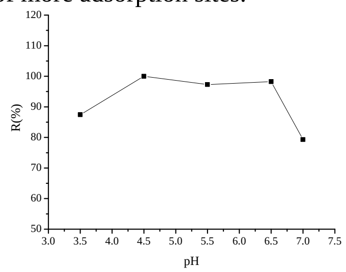
Fig.1. (a) SEM Image of RS, (b) SEM Image of MRS, (c) MRS adsorption.

From Fig.1, it is clear that the MRS shows more wrinkle and specific surface than the RS. The fibre membrane becomes thicker after adsorption. It indicates that the MRS has a more adequate morphology and adsorption effectiveness for Ni(Ⅱ) adsorption.

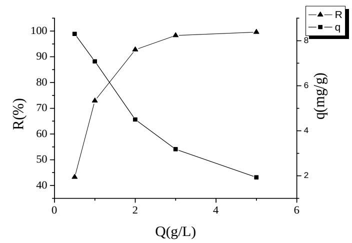
3.2. *Effect of Operating Variables on the Ni(Ⅱ) Adsorption*

Fig.2(a) displays the removal rate values at different pH levels ranging from 3.5 to 7.0. As shown, the Ni(Ⅱ) removal rate increased with rising pH values, reaching about 99.7% at pH 6.5. The removal rate was about 31.8% under same standard conditions by using RS (no presented in Fig). The reasonable reason is that the solution pH affects the adsorbent surface charge consequently affects the adsorption process of Ni(Ⅱ) from aqueous solution. At low pH, the increased number of protons (H^+) in solution on this adsorbent outcompete the Ni(Ⅱ) ions for the available active sites. At moderate pH, there are fewer H^+, thereby allowing more Ni(Ⅱ) ions to be adsorbed to the vacant sites[8].

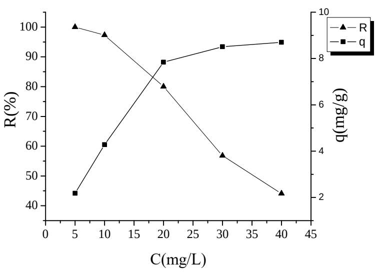
The effect of adsorbent dose on the adsorption of Ni(Ⅱ) onto the MRS is shown in Fig.2(b). It shows that the MRS adsorption capacity (q, $mg \cdot g^{-1}$) decreased from 8.30 to 1.93$mg \cdot g^{-1}$ but the removal rate (R%) increased from 43.3 to 99.7% as the absorbent dose rose from 0.5$g \cdot L^{-1}$ to 5$g \cdot L^{-1}$. It may be due to the increase in adsorbent surface area and availability of more adsorption sites.



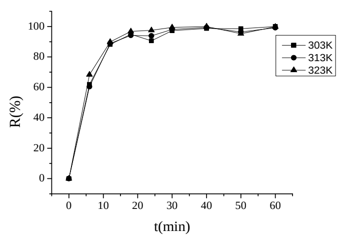
(a) Effect of solution pH level on Ni(Ⅱ) removal rate: dosage =2g L^{-1},



(b) Effect of adsorbent dose on Ni(Ⅱ) removal rate: pH=6.5, C_i=10mg L^{-1},T=303K.



(c) Effect of initial Ni(Ⅱ) concentration on Ni(Ⅱ) removal rate: dosage =2g L^{-1}, pH=6.5, T=303K.



(d) Effect of temperature on Ni(Ⅱ) removal rate: dosage =2g L^{-1}, C_i=10mg L^{-1}, pH=6.5

Fig.2. Effect of operating variables on Ni(Ⅱ) adsorption.

Fig.2(c) shows the influence of initial Ni(Ⅱ) concentration at pH 6.5. Ni(Ⅱ) removal rate decreased but Ni(Ⅱ) adsorption capacity rose as Ni(Ⅱ) concentration increased. With the increase in initial Ni(Ⅱ) concentration from 5mg·L^{-1} to 40 mg·L^{-1}, the Ni(Ⅱ) removal rate at equilibrium decreased from 99.7% to 44.1%, adsorption capacity increased from 2.18 mg·g^{-1} to 8.7 mg·g^{-1}. It may be due to there were more Ni(Ⅱ) ions in the solution as the amount of active sites in the surface of MRS is constant. Besides, the driving force from the concentration gradient increased in higher Ni(Ⅱ) concentration; that is, under the same conditions, if the concentration of Ni(Ⅱ) in solution was increased, then the active sites on the biomass would be surrounded by many more Ni(Ⅱ) ions, so that more sorption would occur[9].

Fig.2(d) shows the temperature at 303K、313K、323K had insignificant influence on adsorption behavior and there was very little increase in adsorption rate with rising in temperature. So adsorption process of Ni(Ⅱ) on MRS was endothermic, but it is less likely to be affected by temperature.

3.3. Kinetic studies

The kinetic process of Ni(Ⅱ) adsorption at optimized conditions was analyzed using the two kinetic models: pseudo-first-order and pseudo-second-order. The mathematical expression is: $\lg(q_e - q) = \lg q_e - k_1 t / 2.303$

For pseudo-second-order: $t/q = 1/(k_2 q_e^2) + t/q_e$

where k_1 is the rate constant for the first-order model for the adsorption process (min^{-1}). k_2 is the rate constant of the pseudo-second-order model (g·mg^{-1}·min^{-1}). q_e is the equilibrium loading of sorbate on sorbent (mg·g^{-1}).

The kinetic parameters for the two models are calculated and shown in Table1. The pseudo-second-order kinetic plot showed a better fit to the data.

Table1 Kinetic parameters for Ni(Ⅱ) onto MRS

Kinetic models		pseudo-first-order			pseudo-second-order		
parameters	q_e(exp)	q_e(cal)	k_1	R^2	q_e(cal)	k_2	R^2
values	7.842	6.217	0.120	0.969	7.985	0.076	0.998

Conditions: initial Ni(II) concentration, 20 mg·L^{-1}; T= 303K; adsorbent concentration, 2g·L^{-1}; pH = 6.5.

3.4. Isotherm studies

Generally, there are two mathematical expressions commonly used to describe the isotherm of the adsorption, Langmuir and Fruendlich equations, respectively.

Langmuir: $C_e / q_e = 1/(q_m k_c) + C_e / q_m$ Fruendlich: $\lg q_e = \lg k_f + \lg C_e / n$

where q_m (mg·g^{-1}) is the theoretical monolayer saturation capacity or maximum adsorption and k_c is Langmuir constant related to the energy of sorption (L·mg^{-1}). k_f (L·mg^{-1}) and 1/n are the Freundlich constants related to sorption capacity and sorption intensity respectively. The parameter values are shown in Table 2.

Table 2 Isotherms constants and correlation coefficients

T/K	Langmuir			Freundlich		
	q_m /(mg·g^{-1})	k_c	R^2	n	k_f	R^2
303	9.17	2.250	0.992	5.5970	5.58	0.897
313	10.45	2.241	0.995	5.2924	6.25	0.970

Conditions: adsorbent concentration, 2g·L^{-1}; pH= 6.5

The most satisfactory prediction of Ni(Ⅱ) adsorption onto MRS was provided by the Langmuir model, as it rendered the highest correlation coefficient (R).

3.5. Thermodynamic studies

Thermodynamic parameters such as the changes in activation enthalpy (*ΔH*), entropy (*ΔS*), and Gibbs free energy (*ΔG*), were calculated according to the following equations to describe the thermodynamics of Ni(Ⅱ) adsorption from aqueous solution: $\Delta G = -RT\ln k_1$; $\Delta G = \Delta H - T\Delta S$. And the results are shown in Table 3.

Table 3 Thermodynamic parameters

T/K	ΔG(kJ·mol^{-1})	ΔH(kJ·mol^{-1})	ΔS(J·mol^{-1}·K^{-1})
303	-2.042	0.277	5.827
313	-2.100		

It is clear the value of *ΔG* was negative suggesting that the adsorption process involved was spontaneous. The positive value of *ΔH* confirmed that the reaction is endothermic and consequently consumes energy.

Chemisorption is the main Ni(Ⅱ) adsorption process according to thermodynamic parameters. The adsorption mechanism may be the functional groups like hydroxyl in the straw contains oxygen atoms with high electronegativity, forming complexation between oxygen atoms and Ni(Ⅱ) ions. RS is mainly composed of lignin, cellulose, hemicellulose, and the modification by $ZnCl_2$ can remove hemicelluloses, lignin, lower crystallinity[6]. So the modification method can improve Ni(Ⅱ) removal rate.

3.6. X-ray photoelectron spectroscopy analysis

The XPS is very much useful in species identification and relative abundances. It is evident that the biosorbent consists of two major elements—carbon and oxygen (Fig.3). The XPS survey spectra of lignocellulosic product loaded with nickel is presented in Fig.4. The presence of adsorbed nickel has been detected on the adsorbent, and the Ni 2p peaks have been analyzed. The Ni 2p peaks sorbed is 856 eV.

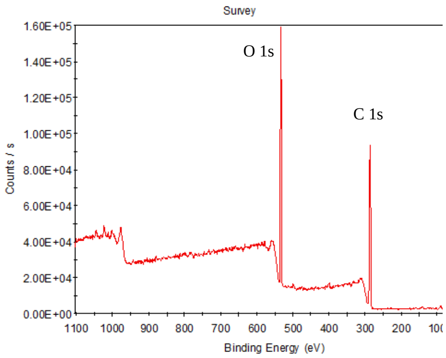


Fig. 3 XPS of biosorbent showing various elements

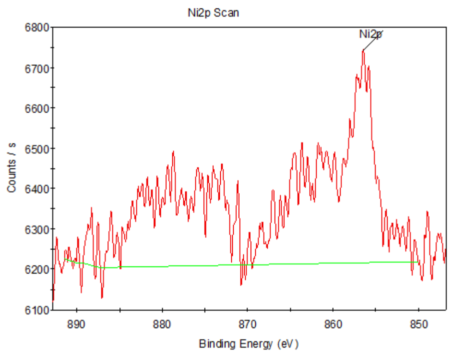


Fig.4 XPS of nickel -loaded adsorbent

4. Conclusions

The study shows that MRS has higher removal efficiency of Ni(Ⅱ) than RS. Removal of Ni(Ⅱ) onto MRS was affected by many factors. The optimal pH and adsorbent dose were 6.5 and 2g·L^{-1}, respectively. Ni(Ⅱ) removal rate increased with decreasing Ni(Ⅱ) concentration and with increasing temperature. The theoretical Ni(Ⅱ) removal rate can reach about 99.7% at the conditions of 303K, pH 6.5, adsorbent dose 2g·L^{-1}, initial Ni(Ⅱ) concentration 10mg·L^{-1}. Equilibrium was achieved in about 18 min under standard conditions. Kinetic date agreed with the pseudo-second-order and equilibrium isotherm data are best described by the Langmuir model. The XPS spectrum of nickel-treated biosorbent reveals that Ni(Ⅱ) is really sorbed onto biosorbent.

Studies show that MRS can be used effectively for removal of Ni(Ⅱ) from aqueous solution. Further studies should be performed to explore the removal of other heavy metal ions.

Acknowledgements

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