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

Ying Wu[a,*], Li Wang[b]

[a]*Department of Chemical and Material Engineering, Hefei University, Hefei 230601,China*
[b]*College of Chemistry and Chemical Engineering, HuNan University, ChangSha 410000, China*

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

* Corresponding author.
E-mail address: wuying@hfuu.edu.cn

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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·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·L^{-1}HCl or 0.1mol·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·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·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.