Pseudo-second-order Model for Sorption of Nickel(II) onto Peat

LIU Zhi-rong, WEI Peng, ZENG Kai, ZHOU Li-min
(Department of Applied Chemistry, East China Institute of Technology, Jiangxi Fuzhou 344000, China)

Abstract: Peat contains many functional groups, such as alcohols, aldehydes, acids, and phenolic hydroxides which can be involved in chemical bonding with metallic ions. The use of peat for removal of nickel from aqueous solution has been investigated at various aqueous pH values by means of liquid scintillation counting. The present research shows that the ability of binding Ni on peat increases with increment of aqueous pH values and reaches the adsorption equilibrium rapidly. A reasonable kinetic model, pseudo-second-order model, has been developped and fitted for sorption of nickel(II) onto peat. The pseudo-second-order model provides a high degree of correlation with the experimental data for the sorption of nickel on to peat.

Key words: nickel-63; peat; sorption; liquid scintillation counting; pseudo-second-order model
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Peat is indeed a complex myriad of chemical systems. Because of the polar character of peat, the adsorption/exchange capacity of peat for metal ions is potentially very high. Batch experiments using peat for the removal of nickel from wastewater have been studied by Su H J[1].

Despite the growing research effort in recent years there is still no consensus concerning sorption-binding model for nickel on peat. In the present study a kinetic analysis about the sorption of ^{63}Ni ions onto peat has been presented in order to establish kinetic mechanism. The pseudo-second-order equation was used to predict sorption rates[2-5].

1 Materials and methods

Peat from Ireland was dried at a temperature of 105℃ for 24 h and then screened though a 14 mesh sieve before being used. The elemental analysis of peat (mass percentage) is 54.27% of Carbon, 5.69% of Hydrogen, 39.34% of Oxygen, 0.70% of Nitrogen respectively. The elemental content of peat is a function of humification and mineralization, the value of salinity is lower at H∶C=1.26∶1 (molar ratio), while the value of decomposition is higher at C∶N=90.45∶1 (molar ratio).

An amount of ^{63}Ni (Aldrich Co.) was dissolved in sulfuric acid, then mixed with stable Ni ($NiSO_4$). After pH value of the solution was adjusted to 6.0, the solution was stored in volume conical flask. The final concentration was 10 000 μg/mL and specific activity was 5μCi/mL. All solution used in this study were diluted with distilled water as required.

Liquid Scintillation Counting (LSC) was used to analyze the concentration of Ni of 12 mL scintillation solution (5 mL ethanol, 7 mL β-PBD) was added into 0.5 mL undeterminate solution, and then the flasks of solution were shaken and analyzed in LSC spectrum (Beckman LS1800) after 2 hours stillness.

The sorption of nickel ions on to peat was studied by batch experiments. All the tests were done in capped conical flasks by suspending the peat in Ni solution, adjusting the pH value to required value by means of hydrochloric and potassium hydrogen phthalate buffering solution and mixing on a shaker with a constant speed. Samples were withdrawn at suitable time intervals, filtered through membrane filter and then analyzed with LSC method. Uptake values were calculated using the equation

$$q_t = \frac{(C_0 - C_t)V}{m_s} \quad (1)$$

Where: q_t the uptake of Ni onto peat at time, t mg/g; C_0 - the initial concentration of Ni, mg/L; C_t - the concentration of Ni at time, t mg/L; V - the volume of the solution, L; m_s - the dry mass of peat, g.

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作者简介: 刘峙嵘 (1969年生), 男, 博士, 副教授; 通讯联系人: 曾凯; E-mail: zk19831125@163.com

2 Results and discussion

Uptake of Ni at varying pH value and time are presented in Fig. 1. Ni can be easily chelated and exchanged with peat in aqueous solution. The capacity of peat for binding Ni is excellent. 60 percent of ^{63}Ni may be bound by peat after 5 mins contact time. The amount of Ni on peat increases with increase of time. While the exchange process reaches equilibrium, the uptake of Ni on peat keep at equilibrium value. There are two different steps in absorption process of Ni on peat possibly. ① at first there are such huge free active sites in peat which may react with Ni that chemisorptions will reach a peak rapidly; ② secondly the adsorption of Ni onto peat comes to a balance after they have been shaken after 60 mins agitation.

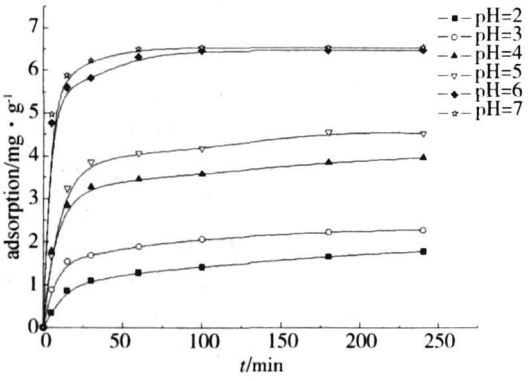

Fig. 1 Adsorption of ^{63}Ni in peat as a function of time and pH

From Fig. 1, it also shows the uptake of Ni increases with increase of pH value and vice versa. We explain that Ni, one of transition metallic ions, has the same empty orbit as hydrogen ion and tend to accept isolated electrons from O and N. Moreover H^+ combines peat more easily than Ni among low pH value. Although carboxyl, hydroxyl groups of peat may be protonized by H^+, probably it will magnify electrostatic repulsion and hinder conjugation between ^{63}Ni and free polar functional groups of peat. If the value of pH overruns the range of 4 to 9, Ni tends to hydrolyze, which is not favorable for sorption.

Since the physicochemical property of peat is hard to describe, pseudo-second-order model is applied for analyzing the process of Ni onto peat during agitation. The rate limiting step may be chemisorptions involving valency forces through the exchange of electrons between covalent nickel ion and peat. Initially it must be assumed that the whole process follows pseudo-second order similar to Langmuir sorption equation.

The peat-nickel reaction may be represented in the following way

$$2\,\text{Peat—H} + Ni^{2+} \Leftrightarrow (\text{Peat})_2Ni + 2H^+ \qquad (2)$$

Where: Peat-H are the polar sites on the surface of peat.

The rate expression for the sorption can be described as:

$$\frac{d(\text{Peat—H})_t}{dt} = k_t\,[(\text{Peat—H})_0 - (\text{Peat—H})_t]^2 \qquad (3)$$

Where: $(\text{Peat-H})_t$- the number of active sites of peat occupied on the peat at time, t; $(\text{Peat-H})_0$- the number of equilibrium sites available on the peat.

The kinetic rate equations for Ni of sorption onto peat can be rewritten

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \qquad (4)$$

Where: k- the rate constant of adsorption, g/mg min; q_e- the amount of Ni adsorbed onto peat at equilibrium, mg/g; q_t- the amount of Ni adsorbed onto peat at any time, t, mg/g.

After separating the variables and integrating this for the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t = q_t$. Equation (4) can be expressed as:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \qquad (5)$$

Equation (5) is the integrated rate law for a pseudo-second-order reaction. Equation (5) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad (6)$$

Equation (6) is manipulated into explicit function of equation (7)

$$q_t = \frac{kq_e^2 t}{1 + kq_e t} \qquad (7)$$

Differentiating and limiting equation (7) into

$$\lim_{t\to 0}\frac{dq}{dt} = \lim_{t\to 0}\frac{kq_e^2}{(1 + kq_e t)^2} = kq_e^2 \qquad (8)$$

h can be regarded as initial sorption rate since $t \to 0$, therefore

$$h = kq_e^2 \qquad (9)$$

Combining equations (7) and (9) will obtain a linear form

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \qquad (10)$$

According to the least square fitting method the constants can be determined experimentally by plotting of t/q_t against t. h, q_e may be deducted from Equation (10). $1/h$ or $1/kq_e^2$ is the intercept of straight line and $1/q_e$ is the slope of it.

Substituting the data of Fig. 1 into t/q_t, we draw Fig. 2. Fig. 2 shows a plot of Equation (10) for the sorption of nickel ions with peat. The results demon-

strate a highly significant linear relationship between t/q and t. The data shows good compliance with the proposed pseudo second ordermodel.

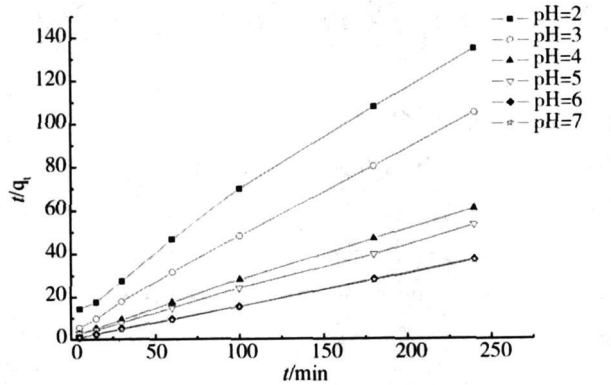

Fig. 2　Pseudo-second-order sorption kinetics of nickel ions on peat for effect of pH

3　Conclusions

Peat has strong affinity to ^{63}Ni in aqueous solution, and the reaction process is fast. The pH value of aqueous solution has great influence on the sorption of Ni. The kinetics of sorption onto peat is followed pseudo-second-ordermodel perfectly.

References:

[1] SU H, ZHAO Y, LI J et al. Biosorption of Ni^{2+} by the surface molecular imprinting adsorbent[J]. Process Biochemistry, 2006, 41: 1422－1426.

[2] GOSSETT T, TRANCART J L, THEVENOT D R. Batch metal removal by peat: kinetics and thermodynamics[J]. Water Research, 1986, 20(1): 21－26.

[3] HO Y S, MCKAY G. The kinetics of sorption of divalent metal ions onto sphagnum moss peat[J]. Water Research, 2000, 34(3): 735－742.

[4] BROWN P A, GILL S A, Metal removal from wastewater using peat[J]. Water Research, 2000, 34(16): 3908～3916.

[5] HO Y S, JOHN WASE D A, FORSTER C F. Batch nickel removal from aqueous solution by sphagnum moss peat[J]. Water Research, 1995, 29(5): 1327－1332.

假二级反应模型在泥煤吸附 Ni(Ⅱ)中的应用

刘峙嵘，韦　鹏，曾　凯，周利民

（东华理工学院应用化学系，江西 抚州 344000）

摘　要：应用液闪分析手段，简要地研究了 pH值对 ^{63}Ni 在泥煤中吸附的影响。结果表明，^{63}Ni 迅速地被泥煤吸附而达到吸附平衡，水相 pH值的增加有利于泥煤的吸附。^{63}Ni 在泥煤上吸附动力学行为可以很好地用假二级反应进行描述。

关键词：镍－63；泥煤；吸附；液闪；假二级反应

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