Kinetics and thermodynamic studies on sorption of NPs by ECDMZ from aqueous solution

Xiaohong LI and Xuekui HAO*

College of Civil Engineering, Lanzhou Institute of Technology, Lanzhou, China
*Corresponding author’s e-mail: haoxuekui@163.com

Abstract. The sorption kinetics of NPs from aqueous solutions by ECDMZ was researched. The experimental results indicated that the sorption of ECDMZ fits the second order dynamic equation. It is showed that the chemical sorption process should be the main factor of controlling sorption rate. Meanwhile, the thermodynamic of NPs from aqueous solutions by ECDMZ were studied too. The thermodynamic research revealed that the whole sorption was exothermic and spontaneous process. In the studied range of 20~100 mg L⁻¹, Enthalpy change dominated the whole chemical sorption process. Temperature had little effect on the sorption process in the studied range of 288~308 K.

1. Introduction
Zeolites, which are non-toxic, odorless and pollution-free, are widely distributed minerals. Zeolites are mainly studied as adsorvent because they possess properties of sorption and ion exchange and characteristics of satisfactory thermal stability and acid resistance [1]. Although zeolites have favourable sorption properties, the sorption capacity is affected by the blocked pores. To further improve the sorption quantity of zeolites, it is necessary to modify zeolites. In many studies of zeolites as adsorbents, a large number of researchers mainly studied on the preparation of high performance, multi-functional modified zeolites through activation and modification, especially the preparation using alkyl long chain surfactants (such as Hexadecyl trimethylammonium bromide) to modify zeolites [2-5]. A large number of studies showed that zeolites modified with different surfactants can adsorb different organics [6-8].

In the previous study, zeolite was modified using β-cyclodextrin (β-CD) and epichlorohydrin (EPI) [9], which were used as modifier and crosslinking agent respectively. The modified zeolite (ECDMZ) was studied on the sorption quantity of nitrophenols (NPs) from aqueous solution [10]. The results showed that the sorption quantity of ECDMZ was obviously improved, especial p-NP.

The current research task is to further investigate the sorption behaviour of NPs from aqueous solutions on ECDMZ. For estimating sorption mechanisms and characteristics of ECDMZ for NPs, the first order and second order dynamic equation have been used for match experimental data. At the same time, the thermodynamic parameters of ECDMZ for p-NP sorption were determined for estimating the sorption mechanism.

2. Experimental process

2.1. Experimental materials
β-CD was supplied by Binzhou Biotechnology Co., Ltd, Shandong, China; NPs was provided by Beijing Chemical Reagent Corp., Beijing, China. Zeolites belongs to plagiotropic zeolite, from Baiyin, Gansu, China.

2.2. Preparation of ECDMZ
The previous research thesis [9] has described the synthesis process of ECDMZ in detail. Probably the synthetic route was as follows: Firstly Zeolite was activated by HCl at room temperature. Then the activated zeolites were modified by β-CD, which EPI was used as crosslinking agent under acid acidic condition. Finally ECDMZ was washed clear and dried.

2.3. Sorption study
Sorption experiments were operated by the batch of experiments. The detailed exposition was reported in the former research thesis also. The experimental process was as below: The self-made mixture which contained ECDMZ and NPs solution were shaken for a desire time at different temperature. Then the supernatant were centrifuged in order to obtain clear supernatants which were used to measure the residual concentrations by a spectrophotometer [10]. The sorption quantity was calculated by the following equation:

\[ q = (C_0 - C_e) \frac{V}{W} \]  

Where, \( C_0 \) is the concentrations of NPs in the initial solution; \( C_e \) is the equilibrium concentration of NPs after sorption for a certain time in the aqueous solution (mg·g⁻¹); \( q \) is the adsorbed number of milligram of NPs per gram of ECDMZ (mg·g⁻¹); \( V \) is the bulk of NPs solution (mL), and \( W \) is the quantity of sorbent (g).

3. Results and Discussion
3.1. Kinetics study
Sorption kinetics was a common research method to study sorption behaviour. The first and the second order dynamic equations were mainly used to determine the material transfer and the control factor of sorption rate in the sorption process. The kinetic constant (k) was used to determine the sorption rate. Here, those equations were employed to suit experimental results, which were from sorptive equilibrium experiments.

Equation (2) was the formula for the linear transformation [11] of the first order dynamic equation:

\[ \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \]  

Where, \( q_e \) is the adsorbed number of millgram of NPs per gram of ECDMZ at sorption equilibrium (mg·g⁻¹); \( q_t \) is the adsorbed number of millgram of NPs per gram of ECDMZ at \( t \) (mg·g⁻¹); \( k_1 \) is the rate constant of the first order sorption (L·min⁻¹).

Equation (3) was the formula for the linear transformation of the second order dynamic equation:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} \]  

Where, \( k_2 \) is the rate constant of the second order sorption (g·(mg·min)⁻¹).
In Figure 1, the curve of contact time and $q_t$ was used to study sorption equilibrium. It was obviously that the sorption equilibrium quickly arrived at 100 min.

The fitting curves of the first and second order kinetics of NPs on ECDMZ were shown in Figure 2 and Figure 3, respectively. The degree of fitting for the two dynamic equations exhibited favourable linear relationship through comparing Figure 2 and Figure 3. However, the degree of fitting of the second order dynamic equation was more favourable.

In table 1, the correlation coefficients ($r$) from the second order dynamic equation were higher than that from first order dynamic equation. Compared the $q_{e,cal}$ gained from the first and the second order dynamic equations, the $q_{e,cal}$ from the second order were closer to the $q_{e,exp}$. Obviously, the second order perfectly followed the sorption process although the two dynamic equations could describe the sorption process of NPs on ECDMZ.

Table 1. Correlation coefficients and kinetics parameters for the sorption of NPs

| adsorbate | $q_{e,exp} \times 10^{-3}$ (mg⋅g$^{-1}$) | $q_{e,cal} \times 10^{-2}$ (mg⋅g$^{-1}$) | $k_1$ (L⋅min$^{-1}$) | $r$ | $q_{e,cal} \times 10^{-3}$ (mg⋅g$^{-1}$) | $k_2$ (g⋅(mg⋅min)$^{-1}$) | $r$ |
|-----------|--------------------------------------|--------------------------------------|----------------------|-----|--------------------------------------|------------------------|-----|
| p-NP      | 689                                  | 576                                  | 0.045                | 0.9895 | 725                                 | 0.150                  | 0.9984 |
| m-NP      | 537                                  | 451                                  | 0.030                | 0.9807 | 597                                 | 0.101                  | 0.9979 |
| o-NP      | 645                                  | 548                                  | 0.040                | 0.9843 | 695                                 | 0.131                  | 0.9989 |

Notes: $q_{e,exp}$—the adsorbed number of milligram of NPs per gram of ECDMZ experiments, $q_{e,cal}$—the calculated number of milligram of NPs per gram of ECDMZ using kinetic models.
Those results showed that the sorption of NPs on ECDMZ included both physical sorption and chemical sorption, however the chemical sorption dominated. It was shown that the chemical sorption controlled the sorption rate.

3.2 Thermodynamic study
By measuring thermodynamic parameters, the main force of sorption can be inferred, which is helpful to estimate the sorption mechanism. Therefore, the thermodynamic parameters of ECDMZ for p-NP sorption were determined in 20~100 mg·L⁻¹. The all data were used to study the sorption process.

On the basis of the following formulas, Thermodynamic parameters were obtained, respectively [12]:

$$\ln C_e = \frac{\Delta H}{RT} + \ln K_0$$  \hspace{1cm} (4)
$$\Delta G = -nRT$$  \hspace{1cm} (5)
$$\Delta S = \frac{(\Delta H - \Delta G)}{T}$$  \hspace{1cm} (6)

Where, $\Delta H$ is sorption enthalpy (kJ·mol⁻¹); $R$ is the constant of ideal gas state, 8.314(J · (mol·K)⁻¹); $T$ is absolute temperature (K); $K_0$ is constant; $\Delta G$ is sorption free energy (kJ·mol⁻¹); $n$ is coefficients in the Freudlich equation; $\Delta S$ is sorption entropy (kJ·(mol·K)⁻¹).

| $T$ (K) | $C_e/q_e = 0.9025C_e + 72.262$ | $C_e/q_e = 0.7338C_e + 113.95$ | $C_e/q_e = 0.6906C_e + 150.26$ | $q_e = 0.0057C_e^{-0.842}$ | $q_e = 0.0050C_e^{-0.7485}$ | $q_e = 0.0044C_e^{-0.8055}$ |
|---|---|---|---|---|---|---|
| 288 | 0.9959 | 0.9915 | 0.9982 | 0.9989 | 0.9969 | 0.9993 |
| 298 | 0.9915 | 0.9982 | 0.9928 | 0.9969 | 0.9993 | 0.9993 |
| 308 | 0.9982 | 0.9928 | 0.9959 | 0.9993 | 0.9993 | 0.9993 |

Table 2 showed the fitting equations and corresponding parameters of p-NP on ECDMZ at different temperatures. It is shown that the sorption behaviour was well fitted to the Langmuir equation and Freundlich equation at 288K, 298K and 308K.

In table 3, $\Delta H$ and $\Delta G$ was negative, which showed that the sorption process was spontaneous and exothermic reaction. The $\Delta H$ increased with the increase of $q_e$, which showed that the sorption process was distinctly influenced by surface inhomogeneity. The slight change of $\Delta G$ with the change of temperature showed that the effect of temperature on sorption was not significant in the studied temperature range. Negative $\Delta S$ showed that $\Delta H$ was the main driving force of sorption in the sorption process.

| $q_e$ (mmol·g⁻¹) | $\Delta H$ (kJ·mol⁻¹) | $\Delta G$ (kJ·mol⁻¹) | $\Delta S$ (kJ·(mol·K)⁻¹) |
|---|---|---|---|
| 288K | 298K | 308K | 288K | 298K | 308K |
| 0.001 | -22.537 | -22.537 | -22.537 | -0.0653 | -0.0645 | -0.0629 |
| 0.002 | -16.943 | -3.728 | -3.179 | -0.0459 | -0.0457 | -0.0447 |
| 0.003 | -13.677 | -13.677 | -13.677 | -0.0345 | -0.0348 | -0.0341 |

4. Conclusion
The kinetics of NPs on ECDMZ investigated that the sorption of ECDMZ was complex, and included both chemical and physical sorption. The sorption process of ECDMZ preferably comforted to the second order dynamic equation. It was obvious that chemical sorption control the uptake rate of the process. The thermodynamic of p-NP on ECDMZ explained that the overall sorption process was exothermic and spontaneous. Temperature had no significant effect on the sorption process. The sorption process was enthalpy pushing in the studied concentration of 20–100 mg·L⁻¹.
5. References

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