DESIGN OF A TWO-STAGE SORPTION SYSTEM FOR Zn AND Cd REMOVAL ONTO IRON-MODIFIED ZEOLITE - MASS OPTIMIZATION

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ABSTRACT

Removal of Zn and Cd onto iron-modified zeolite (IMZ) in a two-stage reactor has been approached using data from single batch study. Optimization involves application of mass balance equation and Dubinin-Radushkevich isotherm on equilibrium data, in order to minimise the total amount of zeolite required to achieve a specific percentage of heavy metal removal.

Keywords: two-stage reactor, design, sorbent minimization, iron-modified zeolite, heavy metals.

INTRODUCTION

Mass optimization using a two-stage reactor can enhance the zeolite efficiency, minimize its total amount and makes the process more economic. In this study, a two-stage batch sorption design approach, shown in Fig. 1, has been applied on experimental equilibrium data of Zn and Cd removal onto iron-modified zeolite (IMZ).

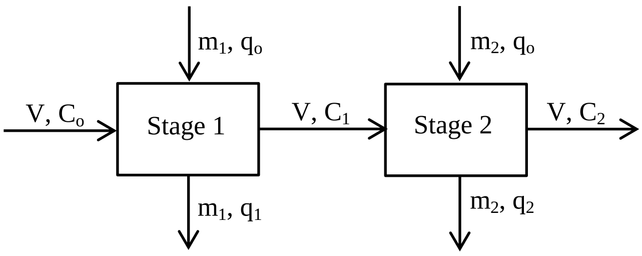

Fig. 1. Shematic diagram of two-stage batch sorption process.

The amount of fresh sorbent was used in each stage to reduce the metal concentration in solution from C_o to C_1 in stage 1 and from C_1 to C_2 in stage 2, thus quantity of sorbed metal ions, q, increases from q_o to q_2. The metal uptake process can be represented by a mass balance equation for each stage:

$$V \cdot (C_o - C_1) = m_1 \cdot (q_1 - q_o) \tag{1}$$

$$V \cdot (C_1 - C_2) = m_2 \cdot (q_2 - q_o) \tag{2}$$

When fresh zeolite is used at each stage, the quantity of metal ions sorbed on zeolite for desired removal efficiency can be obtained by rearranging Eqs. (1) and (2) as follows:

$$q_1 = \frac{V}{m_1} \cdot (C_1 - C_o) \tag{3}$$

$$q_2 = \frac{V}{m_2} \cdot (C_1 - C_2) \tag{4}$$

If the equilibrium metal uptake follows the Dubinin-Radushkevich isotherm (DR), the quantity of metal sorbed can be calculated using the equation:

$$q = q_{cal} \cdot e^{\left(-K_D \cdot \varepsilon^2\right)} \tag{5}$$

where

$$\varepsilon = R \cdot T \cdot \ln\left(1 + \frac{1}{C_e}\right) \tag{6}$$

Combining Eq. (5) with (3) and (4), the amount of zeolite required for the desired removal of metal ions for each stage can be predicted as follows:

$$m_1 = \frac{V}{q_{cal} \cdot e^{\left(-K_D \cdot \varepsilon^2\right)}} \cdot (C_o - C_1) \tag{7}$$

$$m_2 = \frac{V}{q_{cal} \cdot e^{\left(-K_D \cdot \varepsilon^2\right)}} \cdot (C_1 - C_2) \tag{8}$$

Eqs. (7) and (8) can be used to determine the amount of zeolite required for a given initial metal concentration and desired removal efficiency for two-stage sorption system. The aim of this study was to reduce the initial concentration to a value of 99% of C_o. As far as we know, this is the first attempt to apply mass balance equation and DR isotherm in the calculation the zeolite mass for a two-stage reactor.

EXPERIMENTAL

Sample preparation: The iron-modified zeolite (IMZ) was prepared from NZ originated from the Zlatokop deposit, Vranjska Banja, Serbia with particle size of 0.6 - 0.8 mm according to the procedure published previously.[1]

Sorption experiments: The examinations of Zn and Cd uptake were carried out by shaking 1 g of IMZ with 100 ml of aqueous solutions containing initial concentrations for Zn (C_o=1.978-12.371 mmol/l) and for Cd (C_o=2.076-13.942 mmol/l). Experiments were performed at the room temperature, using the batch technique for 24 hours. After equilibration, the suspensions were filtered and concentrations of remaining Zn and Cd ions were determined by ion chromatography.

RESULTS AND DISCUSSION

DR isotherm produced the best fit to the equilibrium data of Zn and Cd uptake on IMZ; the calculated parameters, using the nonlinear regression analysis, are listed in Table 1.

Table 1. Calculated parameters of Dubinin-Raduskevich isotherm for sorption of Zn and Cd onto IMZ.

Metal ion	q, mmol/g	q_{cal}, mmol/g	K_D mol^2/kJ	r^2
Zn	0.433	0.439	0.027	0.988
Cd	0.381	0.362	0.042	0.989

Two-stage batch sorption design approach involves the application of the DR isotherm model and mass balance equation to the experimental data of Zn and Cd removal onto iron-modified zeolite. For optimization of zeolite mass in two-stage reactor, the initial concentration in stage 1, C_1, is divided into 0.1 mmol/l intervals of the range 1.978 – 12.371 mmol Zn/l and 2.076-13.942 mmol Cd/l, and each interval has been marked as system number, N=1,2,3,…128. The equilibrium concentration in stage 2 is determined on the basis of the desired removal efficiency of 99%. For the selected *i)* initial concentration, *ii)* solution volume and *iii)* desired removal efficiency, the total zeolite mass has been calculated using the Eqs. (7) and (8). The results of optimization to obtain the minimum zeolite mass, as well as the zeolite mass in both stages to achieve 99% Zn and Cd removal on IMZ at different initial concentrations, are given in Tables 2 and 3.

Table 2. Calculated minimum zeolite mass in order to achieve the 99% removal efficiency for Zn, based on different initial concentrations at constant volume of 1 l.

System Number	C_o, mmol/l	C_1, mmol/l	Stage 1 m_1, g	C_2, mmol/l	Stage 2 m_2, g	Stage 1+2 m, g
107	12.371	1.2	29.89	0.126	5.90	35.79
89	10.246	1.0	25.33	0.106	5.50	30.84
72	8.051	0.8	20.57	0.081	5.15	25.72
53	6.207	0.6	16.81	0.062	4.62	21.43
36	4.030	0.4	12.07	0.040	4.30	16.37
28	1.978	0.2	7.62	0.020	3.95	11.57

Results show that for both Zn and Cd the required zeolite mass in stage 1, m_1, is higher if compared to stage 2, m_2. This is due to the higher initial feeding concentration in stage 1 than that in stage 2. Total minimum zeolite mass increases with increasing initial metal concentration, and relates tn the S/L (solid/liquid) ratio. Our previous experiment has shown that optimal S/L ratio is up to 20 g/L.[2] This indicates that for initial concentration lower than 6 mmol Zn/l and 4 mmol Cd/l, the implementation of a two-stage reactor is strongly recommended. For higher concentration and same S/L ratio up to 20 g/L, a three-stage reactor is suggested in order to minimize the amount of IMZ.

Table 3. Calculated minimum zeolite mass in order to achieve the 99% removal efficiency for Cd removal, based on different initial concentrations at constant volume of 1 l.

System Number	C_o, mmol/l	C_1, mmol/l	Stage 1 m_1, g	C_2, mmol/l	Stage 2 m_2, g	Stage 1+2 m, g
128	13.942	1.1	35.52	0.139	8.28	47.90
109	11.967	1.0	34.29	0.120	8.36	43.13
91	9.940	0.8	29.91	0.100	8.59	38.51
74	8.084	0.6	26.50	0.081	8.13	34.63
54	5.988	0.5	20.70	0.060	10.23	30.93
36	4.024	0.4	15.00	0.040	7.32	22.32
29	2.076	0.1	11.59	0.020	6.62	18.21

For the same initial concentration and removal efficiency, the required total zeolite mass is lower for Zn than that for Cd, as the amount of sorbed zinc on IMZ is a slightly higher if compared to Cd.

CONCLUSION

The optimization process based on the use of a two-stage reactor, in order to have a highly efficient removal of Zn and Cd onto IMZ, is here described. Our experimental findings show that the two-stage sorption reactor reduces the amount of IMZ. Minimum zeolite mass has been calculated for the two-stage reactor process, in order to achieve the desired removal efficiency.

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