ISSN 1846-6168 (Print), ISSN 1848-5588 (Online)
ID: TG-20171123184728

Original scientific paper

INVESTIGATION ON THE EFFECTS OF PROCESS VARIABLES ON COPPER EXCHANGE ON NaX IN A BATCH STIRRED REACTOR

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Abstract: The aim of this work was to determine the effects of anion type (A), time (*t*), impeller off-bottom clearance (C/H) and solute concentration (*c*) on copper exchange on zeolite NaX in a batch stirred reactor. The experiments were carried out at constant temperature (300 K) and at the same impeller speed (250 rpm). The amount of exchanged copper at examined conditions was measured by UV/Vis spectrophotometer. In order to find the optimal process conditions for copper exchange on the basis of experimental data, Taguchi's method for experimental design were used, applying larger-the-better approach. Beside the optimum experimental conditions this method allowed to define the influence of each process variable on the process conducted. Applied method has shown that the highest copper exchange is achieved at increased solute concentration, when sulphate anion was used, and impeller is positioned at standard position (C/H =0.33). It was also found that solute concentration and anion type have more pronounced impact on process investigated than impeller position and process duration (c > A > c/H > t). For the optimum experimental condition, kinetic data for copper exchange were obtained and tested using the Elovich and the Ritchie kinetic models.

Keywords: batch reactor; ion exchange kinetics; optimisation; zeolite

1 INTRODUCTION

Zeolites are a very promising support for design and preparation of environmentally friendly catalysts. Among others, copper exchanged zeolites are also used as catalysts and could be used for selective ammonia oxidation, carbon monoxide oxidation at low temperatures, toluene removal, wet peroxide oxidation of phenol, etc. [1-4]. Zeolite NaX is a microporous, crystalline solid with a well-defined three-dimensional silica-alumina structure and extra-framework exchangeable sodium cation. It is the synthetic form of naturally occurring aluminosilicate mineral faujasite.

The Taguchi method uses a specifically fashioned orthogonal array consisting of controllable parameters and their variation levels in order to optimise process conditions. For quality assessment this method could use three types of signal to noise (*S/N*) ratio: smaller-the-better, nominal-the-best, and larger-the-better [5]. The advantage of Taguchi method is assessment of optimal experimental conditions with the least number of experiments. Already, this method has been used for process optimization for heavy metal sorption [5-9].

The stirred tank batch reactor is still the most widely used reactor type in the laboratory. It is used for variety of objectives including homogenizing single or multiple phase in terms of concentration of components, physical properties, and temperature. In the solid-liquid system mixing needs to ensure suspension of solid particle and appropriate conditions for mass and heat rate transfer in the solid-liquid interface. Fluid flow pattern in stirred vessel may have considerable effect on the mentioned process outcomes. Flow patterns in the reactor mainly depend upon impeller geometry. When impeller with flat blades is used, the radial flow inside the vessel is generated. In that case, fluid stream is discharged towards the vessel wall and it divides; one portion flows downward along wall and back to the centre of impeller from below, while another portion flows upward toward liquid surface and back to the impeller from above. Fluid flow pattern in stirred reactor, beside the impeller type, depends on impeller off-bottom clearance and impeller size as well [10, 11].

The aim of this work was to investigate the influence of anion type, time, impeller off-bottom clearance and solute concentration on copper exchange on zeolite NaX in order to find optimal process conditions. Process kinetics, at optimal process conditions, is investigated as well.

2 MATERIALS AND METHODS
2.1 Materials

Zeolite NaX (Sigma-Aldrich) was crushed and sieved to obtain particles between 0.071 and 0.090 mm. Solutions containing Cu^{2+} were prepared using the appropriate weight of $CuSO_4 \cdot 5H_2O$, $CuCl_2 \cdot 2H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$. The initial concentrations of copper solutions were checked by the Perkin Elmer Lambda 25 UV/Vis spectrophotometer.

2.2 Taguchi method

In this study, experiments were planed according to Taguchi's L9 orthogonal array, which has nine rows corresponding to the number of experiments and four columns corresponding to the controllable factors, Tab. 1. In this study, anion type (A), time (*t*), impeller off-bottom clearance (*C*/*H*) and concentration of copper solution (*c*) were chosen as controllable factors and their effect on the amount of copper retained on zeolite was investigated. All the selected factors, Tab. 2, had three testing values, represented as level 1, 2 and 3.

In this work larger-the-better characteristic was used:

$$\frac{S}{N_{\mathrm{LB}}} = -10 \cdot \log \frac{\sum_{i=1}^{n} \frac{1}{y_i}}{n} \qquad (1)$$

where S/N represent signal-to-noise ratio, subscript LB is larger the better, n is the number of repetition (three) under the same experimental conditions, and y is a measurement result, i.e. amount of copper retained on the zeolite NaX.

Table 1 Design of experiments

Test	Factor			
	Anion	Time	Impeller off-bottom clearance	Concentration
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Table 2 Controllable factors and associated levels

Factor	Level 1	Level 2	Level 3
Anion type (/)	Sulphate	Chloride	Nitrate
Time (min)	50	30	10
Impeller off- bottom clearance (/)	0.2	0.33	0.46
Solution concentration (mmol/l)	5	10	15

The amount of copper retained on the zeolite, q_t, was calculated as:

$$q_t = \frac{(c_0 - c_t)\cdot V}{m} \tag{2}$$

where c_0 is the initial concentration of copper solution (mmol/l), c_t is the concentration of copper solution at time t (mmol/l), V is the volume of solution (l) and m is the mass of zeolite (g).

The next step in Taguchi method is calculation of average S/N_{LB} ratio of each controllable factor at level i, denoted as S/N_{FL}, in order to determine the optimal conditions:

$$\frac{S}{N_{\mathrm{FL}}} = \frac{\sum_{j=1}^{n_{Fi}}\left[\left(\frac{S}{N_{\mathrm{LB}}}\right)_i^F\right]_j}{n_{Fi}} \tag{3}$$

where $\left(S/N_{\mathrm{LB}}\right)_j^F$ represents S/N_{LB} ratio for factor F on the level i, the superscript j is the j^{th} appearance of the i^{th} level [5]. For the 9 tests, each level for every factor appears 3 times.

2.3 Kinetic models

The Ritchie model is expressed as [12]:

$$q_t = q_e\left[1-\left(\frac{1}{1+k_2 t}\right)\right] \tag{4}$$

where q_e is the amount of copper exchanged in equilibrium – maximum capacity (mmol/g), t is time (min) and k_2 is the rate constant of the Ritchie second-order kinetic model (g/mmol min).

The Elovich model is presented as [13]:

$$q_t = \frac{1}{b}\cdot \ln(1+a\cdot b\cdot t) \tag{5}$$

where a and b are the constants.

2.4 Experimental procedure

Experiments for Taguchi method were carried out in a stirred batch reactor. The glass reactor with the internal diameter of $T = 12$ cm was equipped with four baffles placed at 90° around the vessel periphery. The solution height, H, was equal to internal vessel diameter ($T = H$). The suspension, 1.3 l of copper solution and 5 g of zeolite, was stirred using straight blade turbine, SBT (Fig. 1). Impeller diameter was $d = 6.5$ cm, and its position, i.e. impeller off-bottom clearance (C/H) was varied in range from 0.20 to 0.46 (Tab. 2). As a source of copper, three different solutions with three initial concentrations (Tab. 2) were used. In order to enable comparison of experiments data all studies were performed at the same temperature ($T = 300$ K), zeolite particle size ($d_{\mathrm{P}} = 0.071$-0.090 mm) and at the same impeller speed ($N = 250$ rpm). At defined time (Tab. 2) the samples were taken from the reactor. Prior to the analysis with UV/Vis spectrophotometer, the samples were centrifuged and filtrated.

Figure 1 Straight blade turbine, SBT

Experiment for kinetic investigation was carried out in the same reactor at optimum process conditions defined using Taguchi method. Sampling intervals for this study were chosen according to the ion exchange rate. In the beginning of the process, the ion exchange rate is quite high so the sampling was done more often; later, as the exchange rate decreases, frequency of sampling is decreased as well.

3 RESULTS AND DISCUSSION

One of the goals of this investigation was to find the optimum experimental conditions which provide the highest copper exchange using the lager-the-better quality characteristic. The results for S/N_{LB} ratios, calculated by Eq. (1), along with the amount of copper retained on zeolite (Eq. (2)), are shown in the Tab. 3.

Table 3 Results of experimental part of Taguchi design and S/N_{LB} ratios

Experiment	q_t (mmol/g)	S/N_{LB}
1	1.227	1.777
2	1.603	4.099
3	1.592	4.039
4	1.514	3.603
5	0.688	-3.248
6	0.980	-0.175
7	1.341	2.549
8	1.615	4.163
9	1.027	0.231

The results show that amount retained is in the range from 0.688 to 1.615 mmol/g and S/N_{LB} ratio in the range from −3.248 to 4.163 depending on the controllable factors. From these S/N_{LB} ratios related S/N_{FL} ratios and ranges for each controllable factor were calculated and shown in Tab. 4. Range was used to determine the impact of the controllable factors on the amount of copper retained on zeolite. It was calculated as the difference between the highest and the lowest S/N_{FL} value for each factor. The largest range implied the most effective factor. In this study, the concentration was found to be the most effective factor and it is followed by anion type, impeller position and the time. It could be seen that with increase of the initial concentration there is the increase in the amount of copper retained on zeolite. This is the result of increase in the driving force, which is the concentration of the solution [14]. The impact of the impeller position could be explained by flow patterns generated by the impeller. Generally, the overall fluid flow pattern in the vessel with an SBT impeller consists of two circulation loops and is characterized by a high shear level. [15, 16] As was first observed by Nienow [17], when impeller is set close to the vessel bottom, this "double-loop" flow pattern transforms to "single-loop", i.e. axial flow pattern. This transition occurred at C/H=0.2, where low impeller off-bottom clearance led to flow compression and ultimately to transformation of radial to axial flow pattern. On the other hand, when impeller was set to the highest investigated clearance (C/H=0,46), due to the relative vicinity of the surface, fully developed radial flow caused a slight air intake. This obviously decreased the zeolite surface available for ion exchange and resulted in the lowest S/N_{LB} value. The effect of anion might be explained by the change in Si/Al ratio of zeolite NaX during the exchange [18-20].

Table 4 S/N_{FL} ratios and contribution of each controllable factor

	Factor			
	A	t	C/H	c
Level 1	3.305	2.643	1.921	−0.413
Level 2	0.059	1.671	2.644	2.157
Level 3	2.314	1.365	1.113	3.935
Range	3.246	1.278	1.531	4.348
pC (%)	29.98	4.53	5.28	60.21
Rank	2	4	3	1

Also, the statistical evaluation of factor importance was made using the percentage of contribution (pC) (Tab. 4). Comparing these results with the range results it could be seen that previously obtained order of significance is confirmed. Therefore, every controllable factor, considering the obtained range and pC, was associated with the rank. Factor which has a rank 1 should be utilized first and so on.

From Tab. 4, the optimum operating conditions (highest S/N_{FL} value) could be evaluated and for the present study these conditions are as follows: A1, t1, C/H2, c3 that is solution of $CuSO_4 \cdot 5H_2O$, 50 min for contact time, of-bottom clearance of 0.33 and concentration 15 mmol dm^{-3}.

These process properties, and the same temperature, zeolite particle size and impeller speed, as for Taguchi design, were used for kinetic study. Results obtained in this experiment were fit to the Elovich and Ritchie kinetic model (Fig. 2).

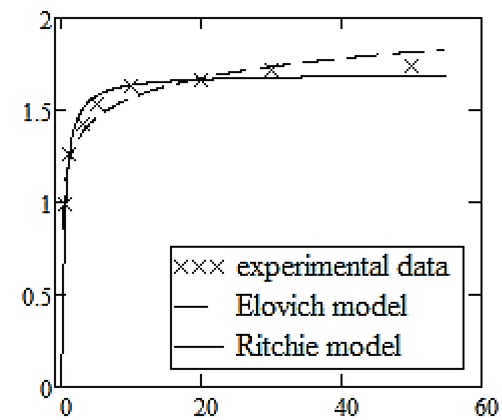

Figure 2 Kinetic data

As it can be seen from Fig. 2, the copper exchange on zeolite NaX better fits with the Ritchie model than the Elovich indicating that tested process is a second-order reaction.

4 CONCLUSION

The effect of anion type (A), time (t), impeller off-bottom clearance (C/H) and solute concentration (c) on copper exchange on zeolite NaX in a batch stirred reactor was studied. According to the Taguchi design analysis, optimal copper exchange is achieved when sulphate anion was used (A1), after 50 minutes (t1), when the impeller is positioned at standard position (C/H2), and at the highest copper concentration (c1). Moreover, the effect of investigated variables was found and in this investigation solute concentration and anion type have more pronounced impact on copper exchange on zeolite NaX than the impeller position and process duration (c > A > C/H > t). For the optimum experimental conditions, kinetic data for copper exchange were obtained and it is found that the Ritchie model describes this data the best.

ACKNOWLEDGEMENT

This work has been fully supported by the Croatian Science Foundation under the project HETMIX (IP-11-2013-8959)

Note: This research was presented at the International Conference MATRIB 2017 (29 June - 2 July 2017, Vela Luka, Croatia).

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