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MATHEMATICAL MODELING FOR KINETICS OF Fe^{3+} EXCHANGE ON PRETREATED ANALCIME**

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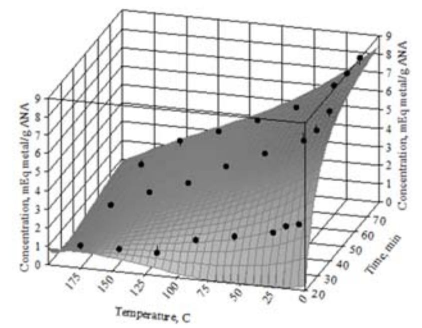
The kinetics of the ion-exchange process with iron on pretreated analcime has been investigated in different conditions of temperature, time and concentration of the exchange solution. The performances of the catalyst were analyzed using the Table Curve software. The mathematical model corresponding to the characteristic equation provides a good arrangement of the experimental points on the responding surface, simplicity of the characteristic equation and a good determination coefficient that is near unity.



INTRODUCTION

There are many natural zeolites that can be used in different chemical processes, due to their properties. This category includes clinoptilolite, analcime, mordenite, ferrierite, heulandite, erionite, chabazite, faujasite, etc. Although it is part of the feldspar group, the analcime has all the structural and chemical characteristics of zeolites. This natural zeolite has a cubic structure, consisting of rings made from 4-6 and 8 tetrahedral cavities that form 16 larger interconnected cavities and a secondary series of 24 smaller cavities. Moreover, some of the sodium ions may be replaced by other ions such as potassium, lithium, cesium, etc. in the composition of the analcime. In Roumania, the analcime is found in an amount of 50-60% in the volcanic tuff.[1,2]

The industrial wastewaters often contain significant amounts of heavy metal ions, which could be harmful to both the environment and to the people. Heavy metals, such as iron, have low atomic density and are usually associated with toxic materials.[3]

Among the procedures applied for removing heavy metals, the ion-exchange on natural zeolites is the most advantageous from economical point of view, as showed in previous studies.[4-10] This method showed remarkable performances when used for removing undesirable ions from residual waters, the ion-exchange capacity being influenced both by chemical and structural properties of the zeolites (composition, porosity, pre-treating, etc.) and the exchange process parameters (ions concentration, temperature, time, etc.).

Several studies dealing with the development of mathematic models that emphasize the performance

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** Supplimentary Information on http://web.icf.ro/rrch/ or http://revroum.lew.ro of various catalysts in different processes revealed that the catalytical behavior is highlighted by the mathematical model developed using Table Curve software- that arranges the experimental data in a three-dimensional area.[11-16] This software is able to make a quick graphical and numerical analysis, providing the dependency relations between physical amounts that characterize the experimental data obtained, thus providing a mathematical model for the study. Furthermore, the software uses around 36.000 approximation procedures which have different equations so that it can establish the ideal approximation equation.[13,14]

Starting from the above considerations the present study is aimed to develop a mathematical model using Table Curve software in order to highlight the performances of the pretreated analcime used for removing of the iron in residual waters by ion exchange method.

EXPERIMENTAL

The volcanic tuff with 50-60% analcime content (Source: Nereju-Vrancea regions-Roumania) was considered for the present study.[1] Firstly, this material was washed with distilled water, dried and screened (ANA). A material with 0.25-0.50 mm grain size was obtained and then mixed with a 1M NaCl solution (1:10 volume ratio) for 24 hours to obtain Na^+ modified analcime (Na-ANA). Further, the sodium analcime was subjected to an ion exchange process with 0.1N salt solutions containing Fe^{3+} ions (1:10 volume ratio) at various temperatures (25, 50, 75°C) for several hours (3-4 hours) to obtain the Fe-ANA(25), Fe-ANA(50) and Fe-ANA(75) samples.

The pH value of the solution before the sorption process was up to 5.0 and after the ion exchange process was 5.7.

The Na^+ cations of the exchange solution were analyzed by flame photometry and Fe^{3+} ions were determined by complexonometric titration.[17]

RESULTS AND DISCUSSION

The behavior of the pretreated analcime was followed in the ion-exchange process with iron (III) ions. We analysed the variation of the exchange capacity of the samples versus time, at three temperatures (25, 50, 75°C). The obtained experimental results were depicted in Figure 1.

In order to establish the importance of the pretreatment of the zeolite, we studied the kinetics of the ion exchange process on untreated analcime at the same temperatures, the data being presented in Figure 2.

As it can be seen in Figure 1, the exchange capacity of the pretreated analcime for iron ions is higher than that for the untreated analcime (Figure 2). Also, the exchange capacity of the pretreated analcime for iron ions at 75ºC is higher than that for the other two temperatures 50º and 25°C, respectively. Probably, this behaviour is mainly caused by the ionic diffusion through the solid pores. Also, it can be noticed that the high amounts of iron retained. It is well known that the Fe^{3+} has a small ion radius and it has acces to certain internal regions of the zeolite structure, having higher exchange rates and higher ion-exchange capacity values. The analcime zeolite consists of a cubic structure consisting of rings of 4-6 and 8 tetrahedral cavities that form 16 larger interconnected cavities and a secondary series of 24 smaller cavities.[1]

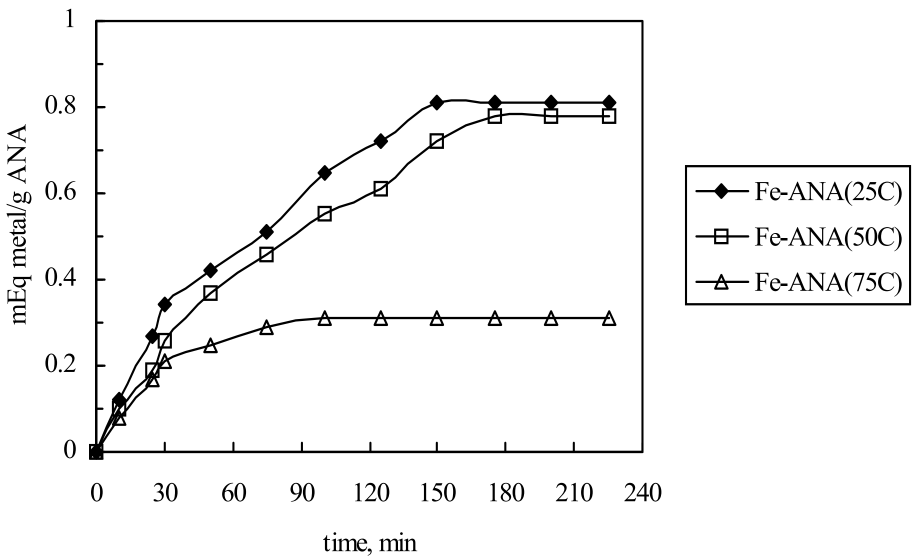

Fig. 1 – Kinetics of ion exchange process for iron (III) ions on pretreated analcime at three temperatures.

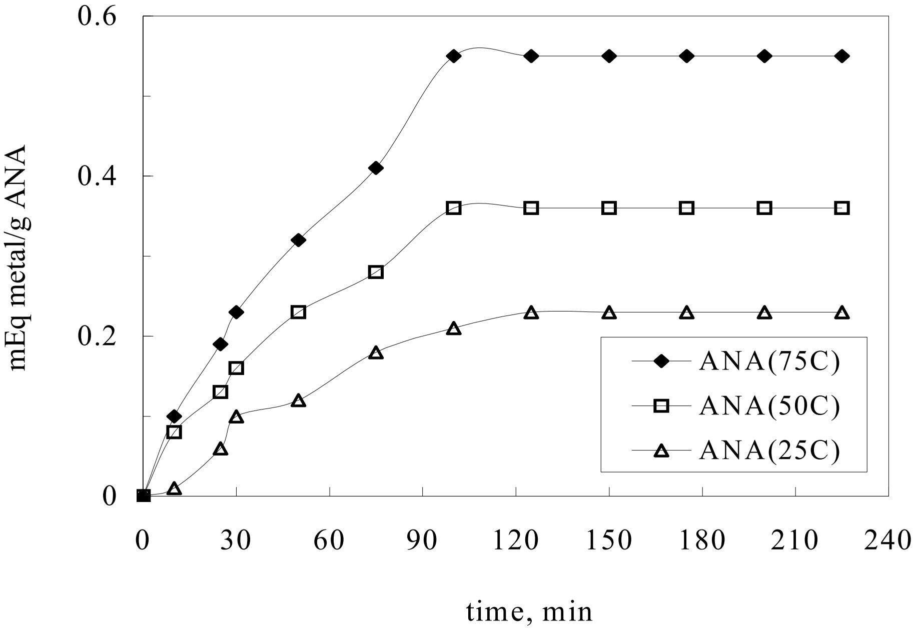

Fig. 2 – Kinetics of ion exchange process for iron (III) ions on untreated analcime at three temperatures.

Table 1

The equations corresponding to the mathematical model for ion exchange process performances

The equation of the mathematical model	The determination coefficient
$z=a+b/x+cy+d/x^2+ey^2+fy/x+gx^3+hy^3+iy^2/x+jy/x^2$	0.9915078717

The obtained experimental data for the ion exchange process of the pretreated analcime with iron at three temperatures were processed by the means of the Table Curve software, by using the general procedure steps like:

- introduction of experimental data;
- graphical representation of the furnished data and selection of the best mathematical model on the basis of the determination coefficient (R^2);
- the simplicity of the characteristic mathematical equation.

The value of the determination coefficient represents the ratio between the spreading degree of the experimental points around the plot of the regression equation and the spreading degree of the same points relative to the arithmetic mean of the own coordinates. Apart from this, a regression function is considered to best approximate the set of the experimental points when the regression coefficient is as close as possible to the unity.[13,14]

By processing the recorded experimental data, the Table Curve software gives 312 equations for the concentration, time and temperature as a relationship between the experimental results and the values calculated by the equations. After a careful selection, the determination coefficient values, the simplicity of the equations and the good arrangement of the experimental points on the response surface were taken into account for the equations in order to obtain all performance criteria.

The most representative equation and the determination coefficient are given in Table 1.

In this equation, the z variable refers to the concentration, *x* variable refers to the reaction time and *y* variable represents the temperature in which the natural material is tested. The significance of each coefficient was determined by t-test and p-values. The larger the magnitude of the t-value and the smaller the p-value, the more significant is the corresponding coefficient. The coefficients of the model given by the software and ANOVA for response surface fit to the experimental results are presented at the end of this paper in the APPENDIX SECTION.

The x-Time (min); y-Temperature (^{o}C) and z-Concentration (mg ion/ml solution) are symbols used in the mathematical model, making evident the catalyst performances in the ion exchange process.

Mathematic model that has the highest value for the determination coefficient and is characterized by a simple equation is presented in Figure 3.

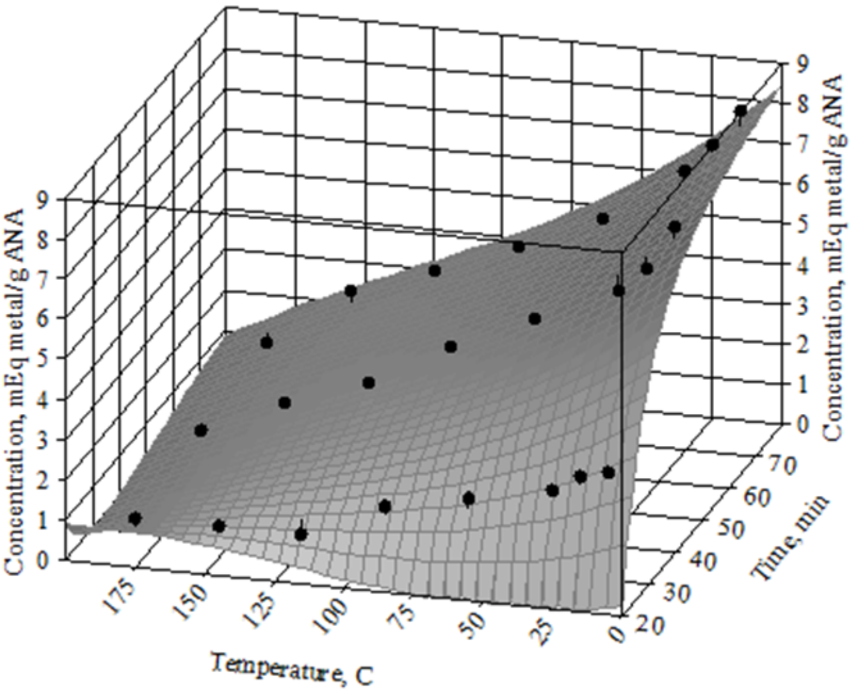

Fig. 3 – Mathematic model for the iron ion exchange on pretreated analcime.

This model shows common characteristics, like a very good positioning of the experimental points on the response surfaces and a correlation coefficient close to unity.

The large R^2 values were evidences for the good relationship, which proved that there was no remarkable variation between the experimental data and the estimated values for performances criteria. All the estimated values were close to each other and showed small variations with the experimental values.

CONCLUSION

The ion-exchange capacity of pretreated analcime for iron at three temperatures (25, 50, 75°C) has been investigated. The best performance of this catalyst was registered at 75°C and was also analyzed by using the Table Curve software. The resulting model showed common characteristics like a very good arrangement of the experimental points on the response surfaces and correlation coefficients close to unity.

The analysis between the experimental results and the value calculated by the equation, resulted in various performance adjustments such as time in terms of process temperature, and had large r-square value, meaning that there was no remarkable variation between the actual and calculated values. Models given by the software and the equations derived in this study gave close estimated values to the experimental results. The best fit model was proposed by the software which possessed the largest r-square value.

This procedure proved to be one of the most rapid and exact possibilities used to describe the influence of the ion-exchange capacity of the pretreated analcime under different conditions (process time, temperature and solution concentration).

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