

ADSORPTION KINETICS AND ISOTHERM MODELS OF Cd(II), Zn(II), AND Cr(VI) BY GEORGIAN NATURAL AND MODIFIED FORMS OF MORDENITE

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Abstract: Environmental pollution with heavy metals is a problem of worldwide importance due to their toxicity and potential health risks. Among the heavy metals found in industrial waters are such toxic metals as Cd(II), Zn(II), and Cr(VI). In this study, the potential of Georgian natural and modified mordenite as a low-cost, eco-friendly adsorbent for the removal of cadmium (II), zinc (II), and chromium (IV) from aqueous solutions is studied. Langmuir and Freundlich isotherms are used to model adsorption data. Studies have shown that the correlation coefficient values (R^2) were best fitted by the Langmuir isotherm. The maximum adsorption capacities are 0.84mg/g, 118.92mg/g and 2.25mg/g for cadmium(II), zinc(II) and chromium(IV) respectively as described by Langmuir isotherm.

Keywords: Mordenite; Isotherm; Heavy metals.

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Introduction

The content of heavy metals in wastewater increases due to human activities [1]. For example: the electrical industry, batteries, pesticides, mining industry, textile industry, petrochemicals, paper production, and use of electrolysis. Heavy metals are not biodegradable [2], and they may be carcinogens [3, 4]. Therefore, the high content of heavy metals in wastewater may cause serious health problems for living organisms. Among the most common heavy metals are zinc (Zn), cadmium (Cd), and chromium (Cr). Even very small amounts of these metals can have dangerous effects on human health [5].

Zeolites are often used for adsorption of heavy metals. Zeolites exhibit different adsorption capacities for heavy metal ions. Natural zeolites are an economical alternative

for the absorption of heavy metals. However, the mechanism of heavy metal adsorption by zeolites has not been well-determined [6, 7]. As a rule, the adsorption mechanism is studied by modeling adsorption isotherms and kinetics of process. All these are conditional estimates of adsorption, which cannot adequately distinguish between the adsorption capacities of different metals.

Adsorption is the most preferred method for removing heavy metals from solutions due to its simplicity, high efficiency, and low cost of operation [8, 9]. Georgian natural mordenite has a high potential for water purification applications. This research aims to study the ability of natural and modified mordenite to remove Cd(II), Zn(II), and Cr(VI) ions from aqueous solutions.

Experimental part

Chemically pure reagents were used for all experiments. Model solutions of cadmium(II), zinc(II), and chromium(VI) (1000 mg/L) were prepared in distilled water using

cadmium chloride, zinc nitrate, and potassium dichromate, respectively. All working solutions were prepared by stepwise dilutions of the stock solution, from 5 to 200 mg/L. The pH was

adjusted with 0.1 M hydrochloric acid or 0.1 M sodium hydroxide solutions. Experimental processes included complete adsorption studies of Cd (II), Zn (II), and Cr (VI) cations on natural and modified mordenite, equilibrium, isothermal modeling and kinetic analysis of adsorption processes.

The adsorption experiment was performed by adding 50 ml of metal model solution to 1 g

of sorbent. Mixing was done for 1 hour at room temperature (22°C). After shaking, the solution was filtered immediately. The metal concentration in the filtrate was determined by the Atomic Absorption method.

The percentage removal of metal ions by natural and modified mordenite as well as the adsorption capacities were calculated from the following equation:

$$E = \frac{(C_0 - C)V}{m} \quad [10] \quad (1)$$

where: C_0 and C – the initial and final (at equilibrium) metal ion concentrations (mg/l);

E – the adsorption capacity (mg/g);

V – the volume of the solution (L);

m – the mass (g) of the adsorbent.

Analysis of adsorption isotherms helps to

identify the mechanism of adsorption.

Adsorption isotherm studies were performed using the Langmuir and Freundlich models, which can be calculated using the following equations:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad [11] \quad (2)$$

The linear form of the Langmuir isotherm is expressed by the equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad [12] \quad (3)$$

The Freundlich adsorption isotherm is an empirical equation used to describe a

heterogeneous system, expressed by the formula:

$$q_e = K_F C_e^{1/n} \quad (4)$$

The logarithmic form of the Freundlich isotherm is given by the following equation:

$$\ln C_e = \ln K_F + (1/n) \quad (5)$$

n indicates how favorable the adsorption process is, K_F is defined as the adsorption or distribution coefficient, it is the amount of

adsorbate adsorbed per unit mass of adsorbent at equilibrium [13].

Results and discussion

Experimental data were analyzed using adsorption isotherm equations. Langmuir and Freundlich isothermal constants (K_L ; $\ln K_F$) are determined and the correlation coefficient (R^2) is calculated. For each metal, the results obtained from the kinetic study of adsorption are used.

The experimental data obtained from the equilibrium studies were correlated with the Langmuir adsorption isotherm. Linear diagrams ($1/C_e$ vs $1/q_e$) were obtained for all three heavy metals in different concentration ranges of metal ions (Cd from 20 to 100 mg/l; Zn from 20 to 100 mg/l; Cr 40 to 100 mg/l). Langmuir

isothermal constants are presented in Table 1.

Table 1. Calculated Langmuir isothermal constants for the removal of cadmium (II), zinc (II) and chromium (VI) from solution.

Heavy metal	Adsorbent	$q_{\max}$ (mg/g)	R^2	K_L (L/mg)
Cd	MOR	0.84	0.97	0.0229
	H-MOR	0.65	0.94	0.0356
	MOR-OH	0.43	0.91	0.0386
Zn	MOR	118.92	0.99	0.0025
	H-MOR	57.12	0.99	0.0057
	MOR-OH	55.04	0.99	0.0057
Cr	MOR	2.25	0.98	-0.047
	H-MOR	2.47	0.95	-0.047
	MOR-OH	2.56	0.95	-0.046

The results in Table 1 show that the Langmuir isotherms for cadmium (II), zinc(II), and chromium(VI) cations are linear. This means that the isotherm fits the experimental results quite well, as evidenced by the value of the correlation coefficient R^2 , whose value ranges from 0.91 to 0.99. Adsorption capacity

for all metals is almost similar for both initial and modified mordenites. Maximum adsorption capacity $q_{\max}$ represents a single-layer coating of the sorbent with sorbate. The best results were obtained on MOR: for cadmium adsorption capacity reaches 0.84 mg/g, for zinc - 118.92 mg/g and for chromium 2.25 mg/g.

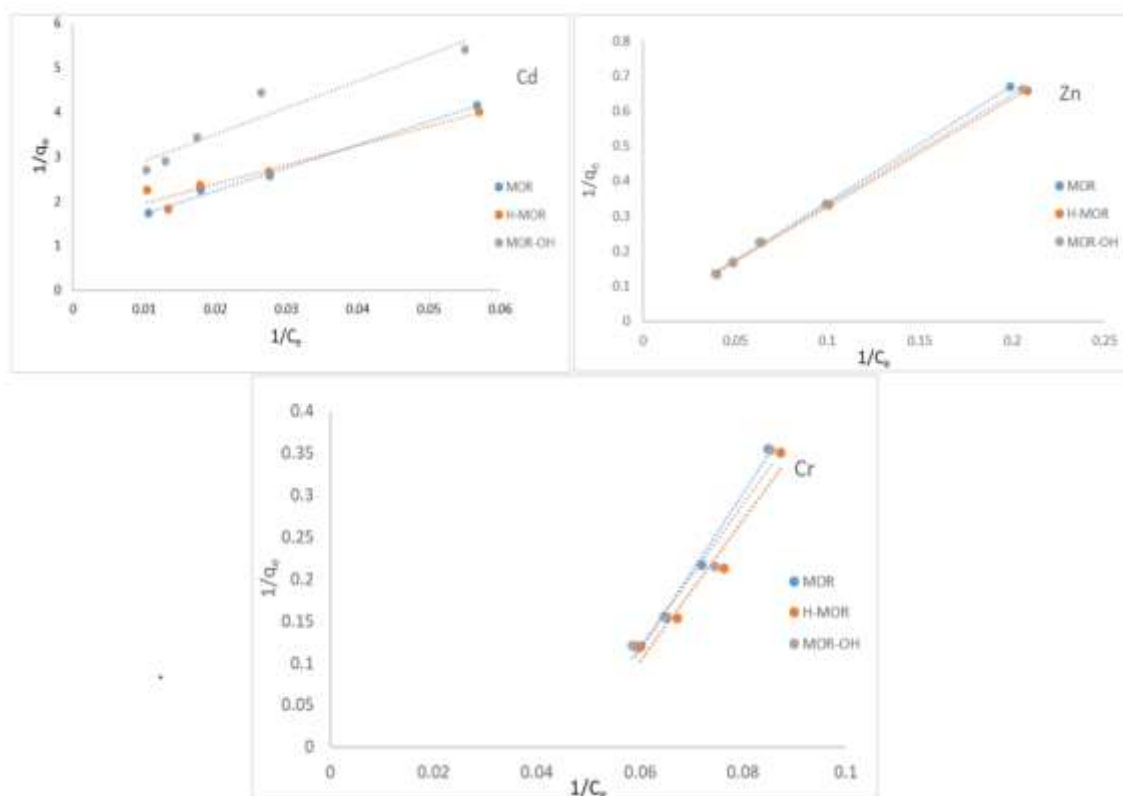


Fig. 1. Linear regression analysis of the Langmuir isotherm for the adsorption of cadmium (II), zinc (II) and chromium (VI) on initial and modified mordenite.

According to the results of adsorption capacity $q_{\max}$, the sorbed metals on all three forms of zeolite will be located in the following order: $Zn > Cr > Cd$.

Fig. 1 shows that in all adsorption studies, the results of all three sorbents vary slightly for each metal. Overall, MOR and H-MOR forms have a higher adsorption capacity compared to MOR-OH. The Freundlich isotherm provides information about the heterogeneity of the

surface and suggests that all adsorption sites are energetically unequal and the adsorption energy is irregular. A line plot is obtained of $\ln q_e$ vs $\ln C_e$ over a specified concentration range for each metal and the values of k and n are calculated. The K value is a measure of the adsorption capacity of the zeolite and it increases in direct proportion to the amount of adsorbed metal.

Table 2. Calculated Freundlich isothermal constants for the removal of cadmium (II), zinc (II) and chromium (VI) from solution.

Heavy metal	Adsorbent	$\ln K_f$	n	R^2
Cd	MOR	-2.887	1.912	0.982
	H-MOR	-2.488	2.478	0.839
	MOR-OH	-2.997	2.287	0.97
Zn	MOR	-1.183	1.021	0.998
	H-MOR	-1.098	1.043	0.998
	MOR-OH	-1.11	1.046	0.998
Cr	MOR	-6.449	0.329	0.998
	H-MOR	-5.849	0.351	0.986
	MOR-OH	-5.752	0.359	0.987

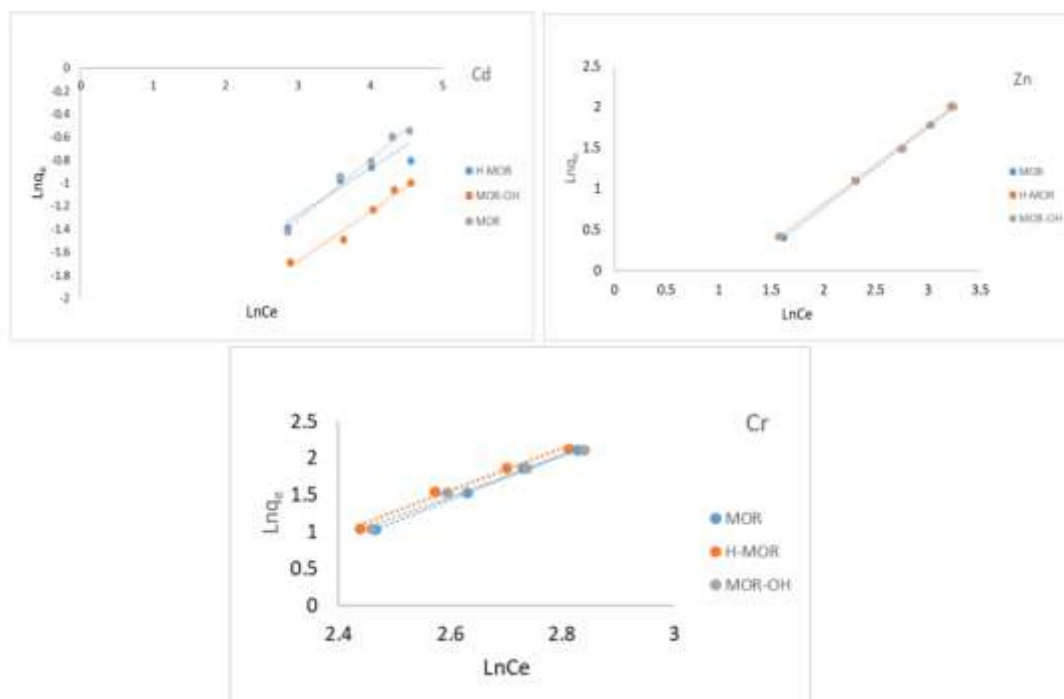


Fig. 2. Linear regression analysis of the Freundlich isotherm for the adsorption of cadmium (II), zinc (II) and chromium (VI) on initial and modified mordenite.

The results obtained from adsorption kinetic studies (Table 2) are consistent with the Freundlich isotherm for cadmium (II), zinc (II)

and chromium (VI) cations. The correlation coefficient (R^2) values range from 0.815 to 0.998. n gives us an indication of how favorable

the adsorption process is on different adsorbents. $\ln K_F$ reflects the distribution coefficient of heavy metals at the moment of equilibrium. When the value of n is greater than one, it allows us to assume that adsorption is favorable at high concentrations but much less at low concentrations.

From the curves in Fig. 2, it is clear that as the initial concentration of heavy metals increases, the amount of metals adsorbed by zeolites also increases.

The Langmuir isotherm fits the experimental data well, as revealed by the correlation coefficient values. For cadmium, the suitability of adsorbents based on the Langmuir

isotherm is as follows: H-MOR has a better correlation coefficient than MOR, and MOR is better than MOR-OH. The effectiveness of all three sorbents for zinc ions is the same ($R^2=0.99$), and the order of adsorption activity for chromium is as follows: MOR>H-MOR>MOR-OH.

The Freundlich isotherm shows less agreement with the experimental data than the Langmuir isotherm. The value range of the correlation coefficient varies from 0.839 to 0.998. This indicates that Langmuir isotherm adsorption data are more accurate than Freundlich, which in turn indicates that the adsorption process is essentially homogeneous.

Conclusion

Based on the conducted research, conclusions have been drawn, which can be formulated as follows:

The results of the equilibrium study showed that natural and modified mordenite could be used as a good adsorbent to remove cadmium (II), zinc (II) and chromium (VI) from solution. The adsorption values of zinc (118.92 mg/g) and chromium (2.25 mg/g) on MOR in 140 and 2.7 times accordingly prevailed the maximum meaning of adsorption of cadmium

(0.84mg/g). According to the results of q_{max} , the sorption of the studied metals on all three forms of zeolite decreases in the following order: Zn>Cr>Cd.

Langmuir and Freundlich isotherm models are used to characterize and evaluate experimental data. A relatively isothermal fit of the correlation coefficients can thus be arranged as Langmuir > Freundlich. Therefore, the experimental results of adsorption fit best with the Langmuir isotherm model.

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