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$[Zn\,(bim)_2(bdc)]_n$ –metal-organic framework: application to strontium ions adsorption in batch and fixed-bed column experiments

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Abstract
A metal-organic framework ($[Zn\,(bim)_2\,(bdc)]_n$, MOF-ZBB) was prepared and applied as an adsorbent for the removal of strontium ions. The influences of several variables such as pH, contact time, and temperature were studied. The Freundlich, Langmuir, and Dubinin-Radushkevich isotherm models, were used for the analysis of equilibrium data. The maximum adsorption capacity by applying the Langmuir equation was 123.451 mg/g at 75 °C with a pH of 7. The thermodynamic study revealed that the adsorption process is endothermic and spontaneous. The pseudo-second-order kinetic model for adsorption strontium ions onto MOF-ZBB better described the adsorption process. The fixed-bed column experiments were carried out at different feed flow rates to investigate the dynamic capacity of the adsorption process. The results revealed a decrease of about 80% in the efficiency of the column by increasing the flow rate from 1 to 4 ml/min.
Keywords: Strontium ions removal, Metal-organic frameworks, Batch and column studies.

Introduction
Decontamination of Sr^{2+} ions from aqueous solutions can be accomplished utilizing various procedures, among them adsorption is considered to be one of the most appropriate techniques. Recently, a new class of crystalline and porous coordination polymers, entitled metal−organic frameworks (MOFs), have emerged as effective sorbents in separation technology. Some features such as ultra-high specific surface areas, mechanical stability, chemical tuneability, high porosity, and controllable pore size and shape are attributed to these adsorbents [1]. Herein, we adopt metal cation Zn^{2+} and benzimidazole (bim) and 1, 4-benzene dicarboxylic acid (H_2bdc) to synthesis a mixed ligand metal-organic framework $[Zn\,(bim)_2(bdc)]_n$ (MOF-ZBB). The feasibility of using the synthesized MOFs as adsorbents for removing Sr^{2+} ions from aqueous media was evaluated under different operating conditions, including contact time, temperature, initial concentration, and pH. Several isotherm and kinetic models were fitted to the experimental data to investigate the Sr^{2+} ions adsorption behavior of the $[Zn\,(bim)_2(bdc)]_n$.

Experimental
Preparation of MOF-ZBB sorbent
The synthesis of MOF-ZBB sorbent was carried out by using a simple hydrothermal method. Briefly, benzimidazole (11.8 mg), $Zn\,(OAc)_2.\,3H_2O$ (21.9 mg), 10 (ml) of distilled water, 16.6 (mg) of H_2bdc, and 0.5 (ml) of sodium hydroxide (0.2M) solution were mixed for 35 minutes, then added into an autoclave flask and maintained at 250 °C for 72 hours. Subsequently, at the cooling rate of 2.5 °C /min, the resulting solution was maintained at room temperature for seven days.

Adsorption experiments in a batch system
0.05 g of MOF-ZBB with 20 ml solution of 25 mg/l strontium of appropriate pH level were placed in a water bath shaker at different contact times (10, 20, 30, 40, 50, 60, 70 and 80 min) and different temperatures (25, 35, 45, 55, 65 and 75 °C). Except for temperature-related studies, all experiments were performed at 25 °C. The aqueous solution was filtered, and the concentration of Sr^{2+} ions was analyzed after completing the contact time. The amount and the percentage of Sr^{2+} ions adsorbed onto the adsorbent at a given time interval were determined by using Eqs (1) and (2):

$$q_e = (C_0 - C_e)\frac{V}{M} \qquad (1)$$

$$R\% = \frac{(C_0 - C_t)100}{C_0} \qquad (2)$$

Adsorption experiments in fixed bed column
Fixed bed adsorption was performed in a glass column with a height of 60 cm and an internal diameter of 0.8 cm, each filled with a known quantity (0.05g) of the sorbent. The MOF-ZBB sorbent was contacted with 200 ml of 25 mg/l strontium solution at a flow rate of 2 ml/min then C/C_0 curve versus effluent volume (breakthrough curve) was plotted where C depicts the outlet concentration of strontium from the tube and C_0 is the initial concentration of strontium (25 mg/l).

Results and discussion
Several experiments were carried out at different contact times from 0 min to 80 min, keeping the initial Sr^{2+} ions concentration of 25 mg/l at pH 7, MOF-ZBB sorbent doses of 0.05, and 25 °C. The results showed that the

adsorption of Sr^{2+} ions on MOF-ZBB was rapid for the first 40 min and reached equilibrium within 80 min. To investigate the adsorption kinetics of strontium ions adsorption onto the MOF-ZBB, four equations were fitted to the experimental data. The estimated parameters of the models, along with the correlation coefficients, are shown in Table 1. Results showed that the pseudo-second-order equation could reasonably describe the kinetics of the adsorption process, which indicates that the chemical adsorption is the primary rate-limiting factor during the adsorption process.

Table 1. Parameters of kinetic models for the adsorption of Sr^{2+} on MOF-ZBB.

Kinetic model (Linear form)	Kinetic constants	Values	R^2
Pseudo-first-order	k_1 (min^{-1})	0.0699	0.91
$ln (q_e-q_t) = lnq_e-k_1t$	q_e (mg/g)	14.15	
Pseudo-second-order	k_2 (min^{-1})	0.003	0.99
$t/q_t = 1/k_2q_e^2 + t/q_e$	q_e (mg/g)	12.69	
Intraparticle Diffusion	C	0.5993	0.96
$q_t = k_{id}t^{1/2} + C$	$k_{id}(min^{-0.5})$	1.0178	
Elovich model	β	2.7328	0.97
$q_t = \beta\ ln(\alpha\beta) + \beta\ ln\ (t)$	α	0.14082	

To determine the effect of initial solution pH, 0.05 g of adsorbent was added into 20 ml (25 mg/l concentration) of Sr^{2+} ions solution in the pH range of 1-13 at 25 °C. The adsorption uptake of Sr^{2+} ions by MOF-ZBB adsorbent reached the maximum values at pH 7 and then decreased at pH values greater than seven.

The effect of common interfering cations on the sorption of Sr^{2+} ions was investigated in the presence of 25 mg/l of Ca^{2+}, Mg^{2+}, Na^+, and K^+ at 25 °C. the selectivity coefficients for strontium ion relative to the interfering ions are shown in Fig. 1. As can be seen, the strontium ions could be adsorbed selectively on the MOF-ZBB in the presence of competing cations, and the inhibition order of the four competing cations on the Sr^{2+} ions adsorption onto the MOF-ZBB was determined to be $Na^+ < K^+ < Mg^{+2} < Ca^{2+}$.

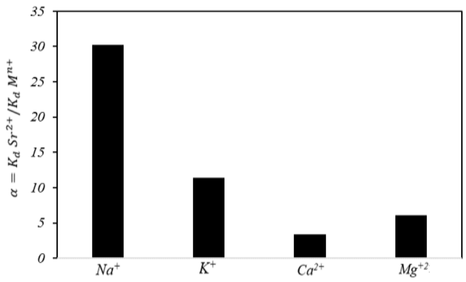

Fig. 1. The selectivity coefficient of the MOF-ZBB for strontium ions relative to the foreign cations.

The temperature effect on the uptake of strontium ions onto the sorbent was studied in the temperature range of 298 to 348 K, at the same time, other parameters were kept constant. The results showed that the Sr^{2+} adsorption on MOF-ZBB adsorbent was promoted at high temperatures. The results show that the adsorption of Sr^{2+} ions on MOF-ZBB was spontaneous and endothermic according to the negative ΔG^o, positive ΔH^o values, respectively.

Three known isotherm models, namely Langmuir, Freundlich, and Dubinin-Radushkevich models, were used to describe the Sr^{2+} ions sorption on the synthesized MOF-ZBB adsorbent. Based on the correlation coefficients, it deduced that the Freundlich model fitted the experimental data better than the Langmuir and D-R models. This suggests that the adsorption process is based on the formation of a heterogeneous composite surface composed of different types of adsorptive sites.

To evaluate the continuous fixed-bed adsorption of strontium onto the MOF-ZBB, the breakthrough studies were carried out by varying the operation conditions, such as the flow rate. The plot of the ratio of effluent to initial concentrations of strontium (C/C_0) versus effluent volume at different flow rates is shown in Fig. 2. As shown in Fig. 2, by decreasing the flow rate, the time of achieving saturation increases. Moreover, by decreasing the flow rate, the mass transfer zone of the column increases, and the fresh or un-adsorbed part of the bed decreases. So, the saturation time of the column would rise and causes an increase in the efficiency of the column. The calculated dynamic capacity at the feed flow rate of 1 ml/min was 64.61 mg/g and 79.84 mg/g at 5%, and 100% Sr^{2+} breakthrough curve, respectively, and the adsorbent column efficiency was obtained 80 %.

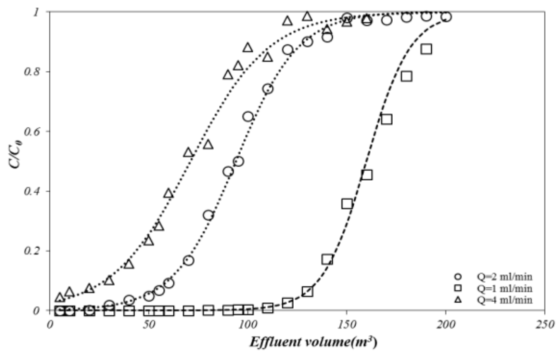

Fig. 2. Breakthrough plot of Sr^{2+} ions on MOF-ZBB.

Conclusions

A porous Zn-based MOF was synthesized, and its novel application for adsorption of strontium ions was investigated. The recommended optimum conditions are pH of 7, contact time of 80 min, and T = 75 °C. The nature of strontium ions sorption was endothermic and spontaneous. The experimental results revealed of strontium adsorption with high linearity follow the Freundlich isotherm model. The pseudo-second-order kinetic model was found to be the most suitable model to describe the adsorption process.

References

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