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THE SORPTIVE PERFORMANCE OF MICROORGANISMS-ZEOLITE SYSTEMS TO REMOVE Cu^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+} AND Pb^{2+}

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The adsorption of Cu^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+} and Pb^{2+} on three types of systems (microorganisms, microorganisms-zeolite, and zeolite) has been investigated. Experimental data have been analyzed by kinetic models including the pseudo-first order, the pseudo-second order and Elovich equations. The film and pore diffusion coefficients were also calculated. The studied ions are desorbed from the microorganisms-systems, after 72 hours, excepting Pb^{2+} which remains adsorbed on bacteria and yeasts systems. The pseudo-second-order equation provides a good fitting to the experimental data points obtained from metal ions adsorption on microorganisms-zeolite and zeolite systems. The zeolite modified with fungi is a more efficient adsorbent than bacteria-zeolite, yeast-zeolite or zeolite for Cd^{2+}. Cu^{2+}, Zn^{2+} and Fe^{2+} were adsorbed with the highest rate by the yeast-zeolite system and Pb^{2+} was adsorbed more efficiently by the bacteria-zeolite system. The adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} onto microorganism-zeolite systems occurs by chemisorption.

INTRODUCTION

The serious environmental problems created by heavy metals motivate the development of new technologies to reduce the contamination with this pollutants.[1-6] A bio-film of microorganisms supported on zeolite seems to be an efficient adsorbent system. Quintelas *et al.*[5] demonstrated that the *Escherichia coli* bio-film on modified zeolite is a very promising way to remove metal ions from effluents, due to the fact that both components have an affinity for metal cations. The cells of microorganisms display the largest surface-to-volume ratio of all the forms of independent life.

The structural polymers in the wall of the microorganisms cell present acidic functional groups like carboxyl, phosphoryl and amino groups, directly responsible for the properties of chemical adsorption.[7] Bio-films are structured communities of microorganism cells enclosed in a self-produced polymeric matrix and adherent to an inert or living surface.[8] The zeolites[9] possess a net negative charge due to the isomorphic substitution of cations in the mineral lattice. They have therefore a strong affinity for metal cations and little affinity for anions and non-polar organic molecules.[10] Tavares *et al.*[11] investigated the behavior of a bio-film of *Arthrobacter viscosus* supported on NaY zeolite in the attempt to remove Cr (VI). Quintelas *et al.*[12] analyzed the biosorption efficiency of a *E. coli* bio-film supported on clay for the treatment of Cr (VI) aqueous solutions. They demonstrated that the microorganisms–zeolite systems they have investigated are efficient adsorbents.

Our research aims to investigate the sorption efficiency of three types of systems: microorganisms (fungi, bacteria and yeasts), microorganisms-zeolite and zeolite in removal of Cu^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+} and Pb^{2+} from synthetic solutions, to applied kinetic models to the obtained experimental data and to establish the adsorption nature.

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EXPERIMENTAL

We procured the natural zeolitic tuff from Stoiana, a village in Cluj county, Roumania (coordinates: 46°40'58″N 23°55'45″E). We have isolated from the sterile substratum of a tailing pond[13] in Bozanta Mare (Maramures County) three species of microorganisms (fungi – *Aspergillus* sp., bacterium – *Sarcina flava* and yeast – *Rhodotorula* sp.). We have supported them on 10 g zeolite in 25 ml nutritive Thorton medium[14] and maintained them to grow for 5 days.

We used a Heindolf Inkubator to stir the vessels with 160 rpm and maintain them at 25^0C. We have then added 25 ml solutions (1000 mg /L) containing Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+} in each vessel, to reach about 500 mg/L as initial concentration of the metal ions.

We have added the metal ions to be investigated on both the systems containing microorganisms alone and the systems containing only zeolite, in order to compare them. We have measured the concentration of the metal ions remained (not adsorbed) after 4, 24, 48 and 72 hours respectively, with a Perkin Elmer AAS 800 Flame Spectrophotometer.

Our measurements with a DRON X-ray powder diffractometer connected to a data acquisition and processing unit to record the XRD patterns allowed for the determination of the parameters of the crystalline network of the zeolite. We have used CuK_α radiation (λ = 1.540598 Å) and a graphite monochromator. The crystal sizes were estimated from the most intense reflection peak [555] by XRD line broadening using the Scherrer equation.[15]

The kinetic models: pseudo-first order,[16] pseudo-second order[17] and Elovich equations[18] were used to test experimental data and to examine the adsorption kinetics.

The pseudo-first order model[16] is one of the most widely used procedures for the adsorption of a solute from aqueous solution. The differential form of the pseudo-first-order equation is shown below:

$$dq_t / dt = k_1 (q_e - q_t) \qquad (1)$$

where k_1 (min^{-1}) is the rate constant of the pseudo-first order sorption, q_t (mg/g) denotes the amount of sorption at time t (min), and q_e (mg/g) is the amount of sorption at equilibrium. After definite integration by application of the conditions: at $t = 0$, $q_t = 0$ and at $t = t$, $q_t = q_t$, the integrated form of Eq. (1) becomes a linear function and model parameters of q_e and k_1 may be obtained from the slope and intercept of log $(q_e - q_t)$ vs. t plot (Eq. 2).

$$\log (q_e - q_t) = \log q_e - k_1 \text{ x } t /2.303 \qquad (2)$$

The pseudo-second order equation[17] is based on the adsorption capacity of the solid phase. Contrary to other models, it predicts the behavior over the whole range of adsorption. The differential form of pseudo-second order based on adsorption equilibrium capacity may be expressed:

$$dq_t / dt = k_2 (q_e - q_t)^2 \qquad (3)$$

where k_2 (g/mg min) is the rate constant of pseudo-second order adsorption.

The integrated form of the pseudo-second order, for boundary conditions ($t = 0$ to t and $q_t = 0$ to q_e) may be expressed:

$$t / q_t = 1 / (k_2 q_e^2) + (1 / q_e)\, t \qquad (4)$$

The plot of t / q_t versus t should give a straight line if pseudo second order kinetic model is applicable and q_e and k_2 can be determined from the slope and intercept of the plot, respectively. Apiratikul and Pavasant[17] demonstrated that the results obtained to the sorption of Cu^{2+}, Cd^{2+} and Pb^{2+} on modified zeolite follow the pseudo-second order kinetic model.

The Elovich equation[18] is one of the most useful models for describing the chemical nature of sorption. In reactions involving chemisorption of adsorbate on a solid surface without desorption of products, the adsorption rate decreases with time due to an increased surface coverage. The Elovich equation can be written as:

$$dq_t / dt = a \exp (- b\, q_t) \qquad (5)$$

where a is the initial adsorption rate (mg/g min) because (d qt / dt) → a as qt → 0 and is related to the rate of chemisorption and b is the Elovich constant, related to the surface coverage[19]. Given that $q_t = 0$ at $t = 0$, the integrated form of Eq. (5) becomes:

$$q_t = (1/b) \ln ab - (1/b) \ln t \qquad (6)$$

The plot of q_t versus ln t should give a straight line if the Elovich equation is applicable and a and b constants can be determined from the slope and intercept of the plot, respectively. Günay *et al.*[18] demonstrated the chemical nature of lead adsorption onto natutal and pretreated clinoptilolite.

In order to compare the validity of each model more efficiently, a normalized standard deviation, Δq is calculated using the following equation:[20]

$$q\ (\%)\quad 100\sqrt{\frac{{}^{\,n}_{i\ 1}\ \ \frac{q_{\exp}\quad q_{cal}}{q_{\exp}}^{\;2}}{n\quad 1}} \qquad (7)$$

where q_{exp} is the experimental metal ion uptake, q_{cal} the calculated amount of metal ions adsorbed and n is the number of data points.

The film and pore diffusion equations (Eq. 8 and 9, respectively) were used to check whether diffusion step controlled to ion exchange process or not.[21]

$$D_f = 0.23\, r_0\, \delta\, q_e / t_{½} \text{ and } D_p = 0.03\, r_0^2 / t_{½} \qquad (8) \text{ and } (9)$$

where D_f is the film diffusion coefficient (cm^2/s), D_p the pore diffusion coefficient (cm^2/s), r_0 the radius of zeolite (0.001 cm), δ the film thickness (0.001 cm, assuming geometry of the spherical particles) and $t_{½}$ is the half time for the ion-exchange process (min). The halt time ($t_{½}$) was calculated from the time requested for the ion-exchange process, which was determined from the quadratic equation $t = A + B\, q_e + C\, q_e^2$, by plloting t versus q_e. δw^2. Argun[21] concluded that both of film and pore diffusions are not the rate-limiting step in the case of adsorption of Ni^{2+} on clinoptilolite.

RESULTS AND DISCUSSION

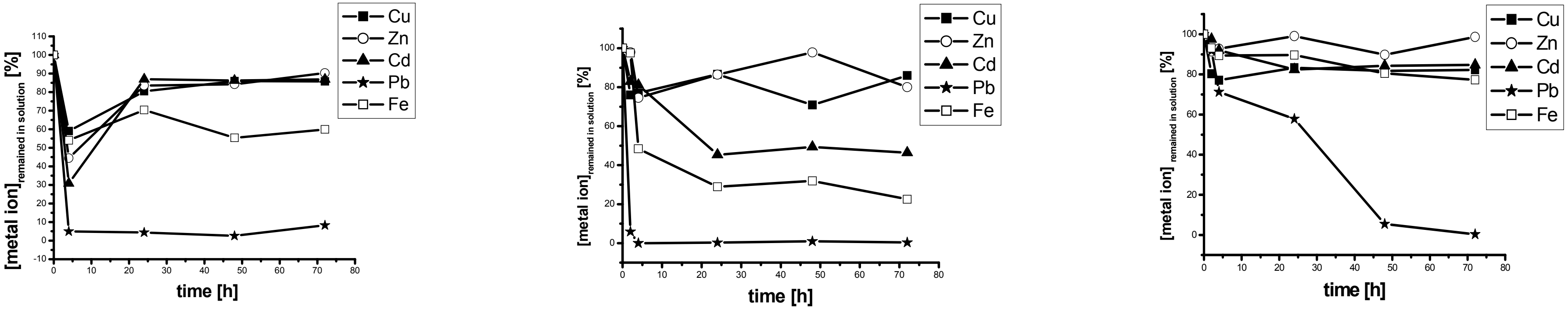
The XRD diffraction analysis has revealed the crystalline structure of zeolite. The average crystallite diameter is 75.74 nm and the root mean square of the microstrain size $<(\varepsilon^2)>^{1/2}{}_{101})$ is 0.002323.

According to Fig. 1 (a) – (c), we remark that all the microorganisms-zeolite systems studied (fungi, bacteria and yeasts) adsorb Pb^{2+} in proportion of 90%, after 72 hours, observation confirmed in the literature.[22,23] The metal ions adsorption on those three microorganisms is quite different. Cu^{2+}, Zn^{2+} and Cd^{2+} are poorly adsorbed by fungi and yeasts (about 15% from the initial concentration), behaviour manifested by Cu^{2+} and Zn^{2+} on bacteria. On the other hand, bacteria adsorbed the highest amount of Fe^{2+} (about 65% in comparison with 40% and 10%, the concentration adsorbed by fungi and yeasts, respectively) and Cd^{2+} (about 55% in comparison with 10% and 8%, concentration adsorbed by fungi and yeasts, respectively). Therefore, the bacteria seem to be the most efficiently adsorbent system for Pb^{2+}, Fe^{2+} and Cd^{2+}. The adsorption behaviour of Cu^{2+} and Zn^{2+} is the same for both fungi and yeasts systems. This behaviour could be explained by the fact that ion-exchange capacity of the bacterium cell wall is higher than that of the fungi and yeasts, depending on the cell structure. A disadvantage of the microorganism systems is desorption of all the adsorbed ions, which occurs after 72 hours of adsorption. Exception to this conclusion is the adsorption of Pb^{2+} on bacteria and yeasts, process in which desorption occurs not.

In order to determine the ion-exchange kinetics of Cu^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+} and Pb^{2+}, the pseudo-first-order and pseudo-second-order kinetic models were examined. The calculated values of q_e (not presented) from the pseudo-first-order kinetics model, using Eq. 2 were noticeably lower than those obtained experimental (not presented) and calculated from the pseudo-second-order kinetics model, using Eq. 4 (Table 1). Additionally, the correlation coefficients (r) obtained from the pseudo-second-order model are higher than those calculated from the pseudo-first-order kinetic model. As a result, the metal ions adsorption on the microorganisms-zeolite and zeolite systems follow pseudo-second-order reaction kinetics. The rate constants of pseudo-second order (k_2) were found to be in the ranges of 1.13 x 10^{-5} and 81.3 x 10^{-5} g/mg min. When the fungi-zeolite system was used, the higher rate constant k_2 was obtained for Cd^{2+}, but when bacteria-zeolite and yeast-zeolite systems were used, the adsorption of Cd^{2+} occurred with lower rate, the rate constants (k_2) being 1.34 x 10^{-5} g/mg min and 3 x 10^{-5} g/mg min, respectively. So, the zeolite modified with fungi seems to be an adsorbent more efficiently than bacteria-zeolite, yeast-zeolite and zeolite for Cd^{2+} removal. The rate constants of Cu^{2+}, Zn^{2+} and Fe^{2+} were higher when the yeast-zeolite system was used (k_2 = 22 x 10^{-5} g/mg min for Cu^{2+}, 5.9 x 10^{-5} g/mg min for Zn^{2+} and 44 x 10^{-5} g/mg min for Fe^{2+}), suggesting that this system is more efficiently than the others for removal of those three metal ions. For Pb^{2+} adsorption, the bacteria-zeolite is more efficient than the other investigated microorganism-zeolite systems, because, on bacteria-zeolite, the rate constant of Pb^{2+} was higher (60.1 x 10^{-5} g/mg min) than on the other systems (43 x 10^{-5} g/mg min for fungi-zeolite, 19.8 x 10^{-5} g/g min for yeast-zeolite and 55.5 x 10^{-5} g/mg min for zeolite).

Elovich equation parameters *a, b* and correlation coefficients, calculated from Eq. 6, are also presented in Table 1. The values of the correlation coefficients are in the ranges of 0.853 and 0.999 (excepting Fe^{2+} in bacteria-zeolite system, which presents the lower correlation coefficient). Teng and Hsieh[19] commented on that the Elovich constant *a* is related to the chemisorption rate and the constant *b* is related to the surface coverage. If we suppose the chemical nature of adsorption and the fact that the constant *a* is related to the chemisorption rate, the constant *a* should increase with rate constant of pseudo-second order (k_2). This means that, in the case of Cu^{2+}, if the k_2 values decrease in order: zeolite > yeast-zeolite > bacteria-zeolite > fungi-zeolite, the values of Elovich parameter *a* decrease approximately in the same order. This correlation is available only for Cu^{2+}, Cd^{2+} and Pb^{2+} and it could not be considered for Zn^{2+} and Fe^{2+}. In these cases, the adsorption process of Zn^{2+} and Fe^{2+} could have a mixed nature (chemical and physical). To elucidate this problem, supplementary experiments are necessary.

On the other hand, the values of the initial adsorption rate constants, *a,* were higher for bacteria-zeolite system, than for the other systems. The highest values for *a* Elovich parameter were obtained for Pb^{2+} and Fe^{2+} adsorption on bacteria-zeolite (0.0191 mg/g min and 0.113 mg/g min, respectively). This means that the chemosorption rate is higher on bacteria-zeolite system than on fungi-zeolite or yeasts-zeolite. The Elovich constant *b* was found to vary between 0.002 g/mg and 0.008 g/mg. The highest value (0.015 g/mg) was obtained for Fe^{2+} adsorbed on the yeasts-zeolite system, suggesting that the coverage of the yeast cells and zeolite particles with Fe^{2+} ions was higher than that achieved for the other ions. By analyzing, the chemosorption rate of Pb^{2+} (*a* Elovich parameter), the highest value was obtained in the case of bacteria-zeolite system (0.0191 mg/g min), on which the highest rate constant k_2 was obtained.



(a)

(b)

(c)

Fig. 1 (a)-(c) – Variation of remained amount of metal ions in time during the adsorbtion process on the microorganism systems: fungi-(a), bacteria-(b), yeasts-(c).

Table 1

The kinetic constants for the metal ions exchange on different systems

	Pseudo-first order kinetic parameters		Pseudo-second order kinetic parameters				Elovich fit parameters				Quadratic fit parameters		
	k_1 [min^{-1}]	r	q_e [mg/Kg]	k_2 x 10^5 [g/mg min]	r	Δq [%]	A x 10^3 [mg/g min]	b x 10^3 [g/mg]	r	Δq [%]	D_f x 10^7 [cm^2/s]	D_p x 10^7 [cm^2/s]	r
fungi-zeolite system													
Cu	0.29	-0.03	2609.8	1.13	0.991	7.3	0.7	1.9	0.985	14.9	10.4	39.1	0.99
Zn	0.49	-0.04	887.2	1.58	0.899	15.8	3.9	7.9	0.878	39	3.4	0.47	0.995
Cd	0.09	0.011	1855	81.3	0.999	3.1	8.9	2.6	0.853	24.2	0.1	0.53	0.963
Pb	0.09	-0.06	1382.1	43	0.999	7.6	6.3	3.3	0.95	18.3	8	5.6	0.895
Fe	0.2	0.02	1254	8.5	0.975	29.5	2.9	3.6	0.988	17.7	5	38	0.963
bacteria-zeolite system													
Cu	0.01	-0.001	1938.6	13.3	0.994	14.2	4.6	2.53	0.973	17.3	10	5.2	0.92
Zn	0.12	-0.01	1966.2	4.53	0.963	51.7	2.4	2.4	0.989	43.6	7.3	36	0.973
Cd	0.09	-0.014	2575	1.34	0.838	49.5	1.5	2.1	0.989	5.12	6	2.3	0.996
Pb	0.05	0.006	1471	60.1	0.994	4.1	19.1	3.7	0.867	21	9.3	62	0.878
Fe	0.26	-0.03	2129.3	7.7	0.984	25.6	113	2.7	0.609	25	10	46	0.945
yeast-zeolite system													
Cu	0.11	-0.015	1534.2	22	0.997	13.5	6.7	3.2	0.955	16.1	8.6	55	0.913
Zn	0.31	-0.048	1403.5	5.9	0.96	23	1.4	3.5	0.978	23.5	7.3	36	0.97
Cd	0.16	-0.025	2143.3	3	0.959	22.1	1.7	2.3	0.987	23.6	6	2.3	0.92
Pb	0.02	-0.033	1714	19.8	0.996	12.4	6.6	2.9	0.946	17.4	9.3	62	0.913
Fe	0.37	-0.052	297.8	44	0.988	16.8	15.7	15.5	0.999	5.5	1.3	42	0.955
zeolite system													
Cu	0.02	0.003	1903.6	25	0.999	9.2	6.4	2.5	0.949	17.1	9.9	4.5	0.899
Zn	0.16	-0.024	188.6	5.8	0.984	19.1	2.2	2.4	0.996	14	7.7	40	0.964
Cd	0.01	0.001	2176	18	0.998	16.8	4.1	2.1	0.968	14.2	12	56	0.9
Pb	0.24	0.032	1487.6	55.5	0.999	17	10	3.3	0.915	18.8	9.4	61	0.88
Fe	0.23	0.035	1898	8.7	0.988	12.5	2.9	2.5	0.997	8.2	9	46	0.944

The film diffusion coefficients (D_f) (Eq. 8) are in the range 10.4 x 10^{-7} and 10^{-8} cm^2/s and the pore diffusion coefficients (D_p) (Eq. 9) are between 39.1 x 10^{-7} and 0.47 x 10^{-7} cm^2/s (Table 1). According to the Michelson *et al.*[24], D_f values should be in the range of 10^{-6} to 10^{-8} cm^2/s for film diffusion to be rate-limiting factor and D_p values should be in the range of 10^{-11} to 10^{-13} cm^2/s for pore diffusion to be rate-limiting factor. From these results it can be concluded that the metal ions diffusion through the film from the microorganism and/or zeolite surface is the rate-limiting step.

CONCLUSIONS

The following conclusions can be drawn from this study.

The microorganisms-systems (fungi, bacteria and yeasts) we have studied adsorb Pb^{2+} in proportion of 90% after 72 hours. Bacteria are the most efficient adsorbent for Pb^{2+}, Fe^{2+} and Cd^{2+}.

All the investigated ions were desorbed from the microorganisms-systems, after 72 hours, excepting Pb^{2+} which remains adsorbed on bacteria and yeasts systems even after 3 days.

The pseudo-second-order equation provides a good fitting to the experimental data points.

The zeolite modified with fungi seems to be a more efficient adsorbent than bacteria-zeolite, yeast-zeolite or zeolite for Cd^{2+} adsorption. Cu^{2+}, Zn^{2+} and Fe^{2+} were adsorbed with the highest rate by the yeast-zeolite system. Pb^{2+} was adsorbed with the highest rate on the bacteria-zeolite system.

The adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} onto microorganism-zeolite systems occurs by chemisorption. To elucidate the nature of Zn^{2+} and Fe^{2+} adsorption (mixed: chemical and physical, or only physical) supplementary experiments are necessary.

The metal ions diffusion through the film generated at the zeolite particles or microorganism's cell surface is the rate-limiting step.

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