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Sensitivity of Freundlich equation constant 1/*n* for zinc sorption on changes induced in calcite by mechanical activation

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Abstract

This work presents an attempt to modify the properties of calcite by mechanical activation in order to enhance its capacity for heavy metal removal. The equilibrium isotherms of zinc adsorption onto the mineral show the data correlate well with Freundlich model. Experiments with temperature changes in sorption tests proved that chemisorption plays the main role in zinc sorption on calcite. The solid-state properties of calcite (surface area, particle size, particle morphology and crystallinity) has been modified by mechanical activation (high-energy milling) and the structure sensitivity parameter, S_A/X (S_A: specific surface area and X: crystallinity) has been used for the characterization of mechanically activated calcite. The good linear correlation ($R = 0.92$) between Freundlich parameter $1/n$ and $\log(S_A/X)$ has been found. The experimental results proved that the mechanically activated calcite is an effective sorbent for Zn removal from water solutions.

Keywords: Zinc; Adsorption; Freundlich; Calcite; Mechanical activation

1. Introduction

The presence of heavy metals in the environment can cause serious environmental pollution problems. Many methods have been proposed for heavy metal removal, e.g. precipitation, membrane filtration, ion exchange and adsorption [1]. Removal of heavy metal based on sorption on mineral surfaces has been suggested as an alternative approach [2–7]. The adsorption process is used especially in the water treatment field and the investigation has been made to determine inexpensive and good adsorbents. Sorption is defined as a surface process irrespective of mechanism, adsorption or precipitation [8]. Both mechanisms involve characteristic reactions of some metals with solid surfaces.

Calcite has been applied for adsorption of Sr, Cd, Mn and Co metals [9–12] as well as Zn metal [13–19]. It is well know that $CaCO_3$ surfaces chemisorb Zn^{2+} ions at low concentrations and higher Zn concentration causes zinc carbonate precipitation. Because of the degree of divalent metals sorption on calcite is sufficiently large it is implied that calcite could act as an important sorbent for metals in calcareous soils an groundwater [15].

The properties of fine particles with a high surface area has led recently to their utilization as sorbents for heavy metals [20]. While many physical properties of these particles are now well understood, the influence on the chemical properties such as adsorption and chemical reactivity remain poorly understood [21]. It is interesting to study how the modification of calcite solid-state properties (i.e. its surface area, particle morphology, crystallinity) influences the process of zinc adsorption.

Mechanical activation of minerals by high-energy milling is a suitable way to influence their solid-state properties. Mechanical activation is an innovative procedure where an improvement in technological processes can be attained mainly via a combination of new surface area and formation of crystalline defects in minerals. The lowering of reaction temperatures, the increase of rate and amount of solubility, preparation of water soluble compounds, the necessity for simpler and less expensive reactors and shorter reaction times are some of the advantages of mechanical activation is not excessive, and accounts for only 15% of the total power consumed by the hydrometallurgical process under study [20].

The transformation of calcite into aragonite and/or the evolution of new surface area was observed by high-energy milling

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[22–27]. It holds for surface energy of any mineral

$$\Delta G_1 = \sigma \, \Delta S \tag{1}$$

where σ is specific surface energy and ΔS is change in overall surface. According to Schrader and Hoffmann [28], for mechanical activation of calcite the surface energy ΔG_1 is approximately equal to 10% of overall Gibbs energy ΔG of calcite. The rest belongs to the energy of lattice defect formation.

The aim of this work was to examine the sorption behaviour of zinc on calcite whose solid-state properties were modified by mechanical activation. Freundlich equation has been applied for description of the sorption process.

2. Experimental

The investigation was carried out with the samples of calcite from Hnúšt'a and Gombasek Slovakia. Both samples have been analysed after dissolution at Institute of Geotechnics. The calcite from Hnúšt'a had the following chemical composition: 51.58% CaO, 0.35% MgO, 1.35% SiO_2, 0.15% Fe_2O_3, 0.12% Al_2O_3 and 42.86% solid rest after annealing.

The chemical composition of the sample from Gombasek was as follows: 54.12% CaO, 0.61% MgO, 0.87% SiO_2, 0.6% Al_2O_3 and 43.8% solid rest after annealing.

2.1. Mechanical activation

The mechanical activation for sample from Hnúšt'a was performed in a planetary mill PULVERISETTE 6 (Fritsch, Germany). The following milling conditions were used: loading of the mill with 50 balls of 10 mm diameter; material of grinding chamber and balls: tungsten carbide; ball charge in the mill 360 g; weight charge in the mill 5 g; rotation speed: 500 min^{-1}; milling time: 0.20, 0.40, 1, 5, 7, 15 and 30 min.

The mechanical activation for sample from Gombasek was performed in a vibratory mill VM 4 (Slovakia) under the following conditions: loading of the mill with 10 balls of 30 mm diameter; material of grinding chamber and balls: stainless steel; ball charge in the mill 1100 g; weight charge in the mill 100 g; milling time: 1, 5, 10, 15, 20 and 30 min.

2.2. Specific surface area

The specific surface area S_A was determined by the low-temperature nitrogen adsorption method. The method belongs to the procedures based on gas adsorption (BET, Harkins–Jura, Kiselev, etc. [29]). The standard Gemini 2360 sorption apparatus (Micromeritics, USA) has been applied.

2.3. X-ray diffraction analysis

The X-ray diffraction of the investigated samples was measured on a DRON 2.0 diffractometer using Fe Kα radiation operated at 10 mA and 25 kV, the time constant was 2 s and the system ran in θ–2θ mode at 2°min^{-1}.

The effect of mechanical activation was evaluated by a decrease of mineral crystallinity (content of crystalline phase) X compared with the reference sample (non-activated), which is assumed to correspond to 100% crystallinity, where X is defined as

$$X = \frac{U_0}{I_0} \cdot \frac{I_X}{U_X} \cdot 100 \tag{2}$$

and U_0 and U_X denote the backgrounds of the reference sample and activated sample, while I_0 and I_X are integral intensities of diffraction lines of the reference sample and activated sample, respectively. This method of crystallinity determination was put forward by Ohlberg and Strickler [30].

2.4. Scanning electron spectroscopy

The scanning electron microscopy was carried out with an equipment BS 340 (Tesla Brno, Czech Republic).

2.5. Sorption test

The sorption was investigated using model solution $ZnSO_4$, which was prepared from chemically pure $ZnSO_4 \cdot 7H_2O$. Initial pH of solutions was 2. pH was regulated by the addition HNO_3 or NaOH. All batch sorption experiments have been performed at temperature 25 °C. Initial zinc ion concentration range was 10–50 mg l^{-1}. The sorbent concentration was 5 g l^{-1}. Residual concentration of zinc metal in solution was determined by the atomic adsorption spectroscopy.

2.6. Freundlich isotherms

The Freundlich model [31] is used to describe the adsorption of gas molecules onto metal surfaces. However, the model has found successful application in many other sorption processes, including sorption from liquid media. We have selected the Freundlich model for analysis of our experimental data. The Freundlich isotherm robustly fits most experimental adsorption–desorption isotherm curves, and is especially good for fitting data from highly heterogeneous sorbent systems, including minerals. In a "batch" aqueous adsorption experiments, the data may be fitted to the Freundlich adsorption isotherm.

The shape of this isotherm strongly suggest that a description of the adsorption is in a form

$$a = k \cdot c^{1/n} \tag{3}$$

where a is the amount of metal ion adsorbed per unit weight, k and n the Freundlich constants and c is the equilibrium concentration of Zn^{2+}. Eq. (3) can be linearized to the form

$$\log a = \log k + \frac{1}{n} \log c \tag{4}$$

The slope of line expressed by Eq. (4) gives the value $1/n$ and intercept of the line gives the value $\log k$. The Freundlich constants for zinc ions sorption and correlation coefficient were calculated.

3. Results and discussion

3.1. Characterization of calcite particles properties

3.1.1. Surface changes

The disintegration of calcite mineral by mechanical activation is accompanied by an increase in the number of particles and by generation of fresh, previously unexposed surface. The dependence of specific adsorption surface S_A of two calcite samples (Gombasek and Hnúšt'a) on the time of mechanical activation is represented in Fig. 1. These traces show that the rate of new surface formation is limited by both time of mechanical activation and type of the mill. The less intensive vibratory mill (2) was used for mechanical activation of calcite from Gombasek and the more intensive milling in a planetary mill (1) has been applied for calcite from Hnúšt'a. The corresponding micrographs for non-activated $CaCO_3$ from Hnúšt'a as well as for the same samples activated by milling for 3 and 15 min are shown in Fig. 2. Besides the effect of disintegration resulting in a greater proportion of finer particles, we can also observe the formation of agglomerates [32], which may have dimensions comparable to those of non-activated particles.

3.1.2. Bulk changes

To appreciate the lattice defects formation in the bulk of minerals several physico-chemical methods can be used [20]. The application of X-ray diffractometry method enables us to investigate the disordering of calcite crystal structure. The changes induced by mechanical activation can be observed by looking at calcite lines broadening and shift and the reduction of line intensity [32]. Crystallinity changes have been calculated according to the formula (2) and were given in dependence with milling time in Fig. 3. More severe decrease in crystallinity was observed for $CaCO_3$ mechanically activated in a planetary mill. However, the phase transformation of calcite into aragonite has not been observed during our milling experiments.

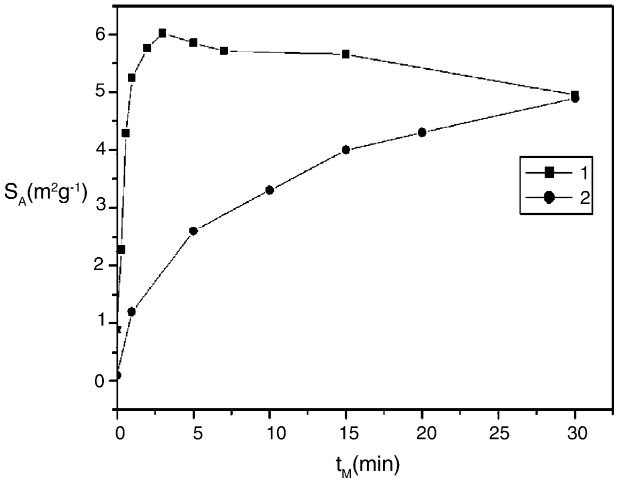

Fig. 1. Specific surface area, S_A, vs. milling time, t_M: (1) planetary milling and (2) vibratory milling.

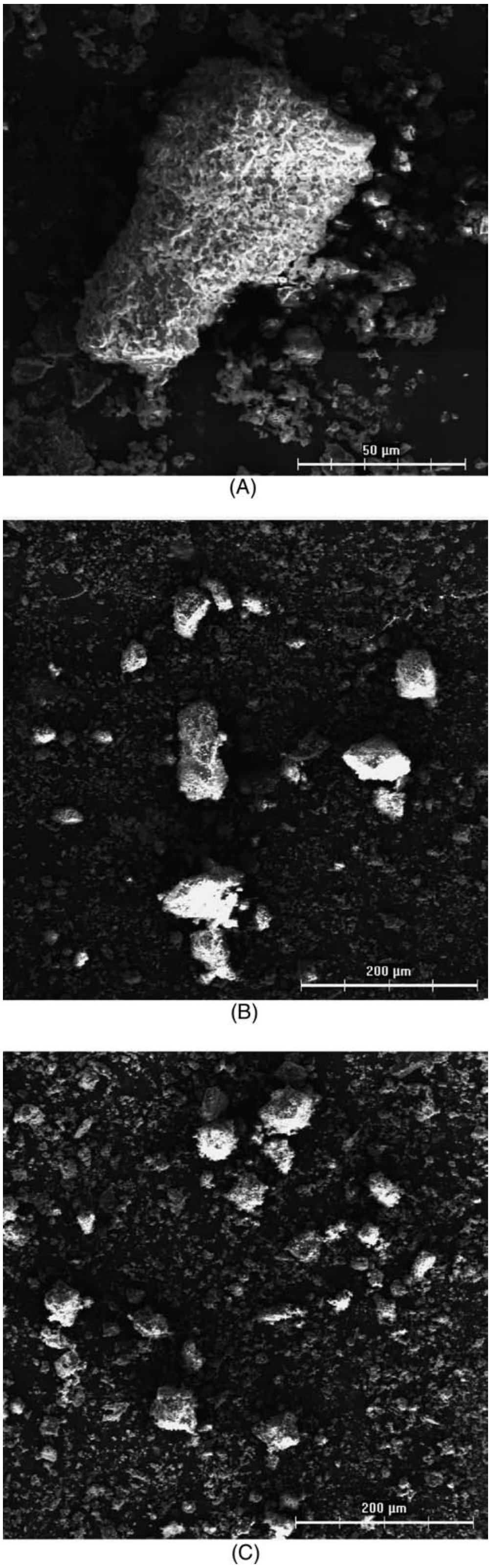

Fig. 2. Scanning electron micrographs of calcite Hnúšt'a milled in a planetary mill, milling time: (A) 0 min, (B) 3 min and (C) 15 min.

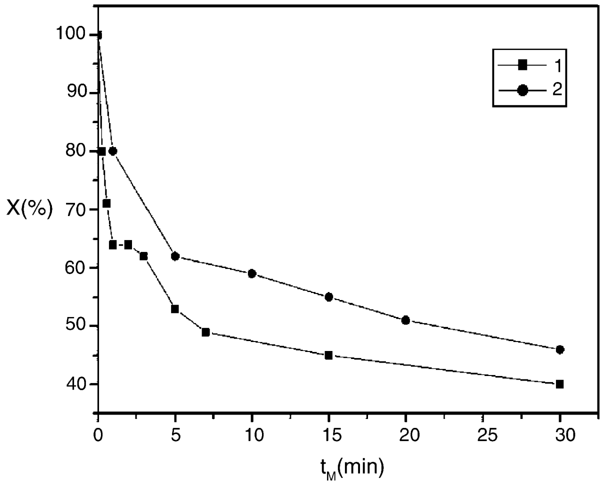

Fig. 3. Crystallinity, X, vs. milling time, t_M: (1) planetary milling and (2) vibratory milling.

3.1.3. *Structure sensitivity parameter*

It was Senna [33] who analysed the effect of surface area and the structural disordering on the reactivity of mechanically activated minerals. A concept of effective surface area was defined as a geometrical controlling factor for a chemical reaction involving powdery materials. Tkáčová and Baláž [34] introduced the complex parameter, which characterizes the overall disordering of solid by milling. This parameter defined as S_A/X, describes the influence of the surface area increase and the crystallinity decrease on chemical processes. In Fig. 4, the changes of this parameter with the milling time are given. In accord with plots in Figs. 1 and 3 a strong dependence on milling conditions is obvious.

3.2. *Characterization of zinc sorption process*

3.2.1. *Dependence on milling time*

The dependence of the zinc uptake E on milling time for planetary and vibratory mill and corresponding surface and bulk changes of calcite during mechanical activation are given in Table 1. More drastic changes in surface and bulk of calcite samples induced in mineral by planetary milling cause the higher zinc uptake in comparison with less pronounced effect of vibratory milling. Generally, there is a strong evidence of positive influence of the overall disordering of calcite by milling on zinc uptake during sorption experiments as manifested in Fig. 5.

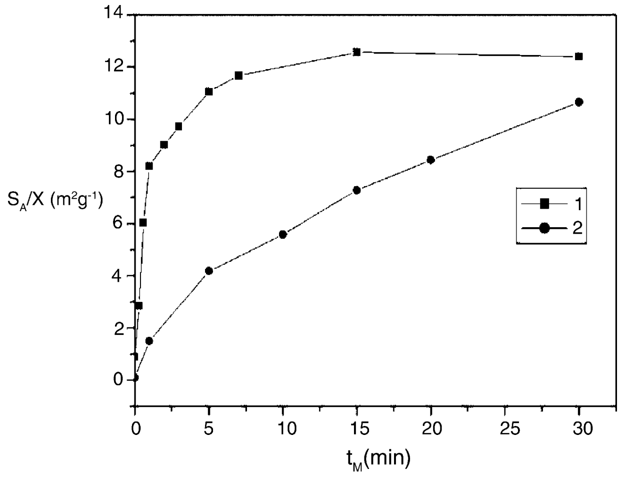

Fig. 4. Structure sensitivity parameter, S_A/X, vs. milling time, t_M: (1) planetary milling and (2) vibratory milling.

Table 1

Zinc uptake, E, specific surface area, S_A, crystallinity, X and S_A/X ratio for calcite milled in a planetary and vibratory mill, respectively, t_M—milling time

Mill	t_M (min)	E (%)	S_A (m^2 g^{-1})	X (%)	S_A/X (m^2 g^{-1})
Planetary	0	35	0.9	100	0.9
	0.6	59	4.3	71	6.1
	3	65	6.0	62	9.7
	15	69	5.7	45	12.7
	30	85	4.9	40	12.4
Vibratory	0	30	0.1	100	0.1
	10	40	3.3	59	5.6
	15	49	4.0	55	7.3
	30	52	4.9	46	10.7

3.2.2. *Effect of temperature*

It is known from literature [1] that if sorption is governed only by physical phenomena an increase in temperature will be followed by a decrease in sorption capacity. We have studied the temperature effect for zinc sorption on calcite at 25, 35 and 50 °C. Fig. 6 shows that zinc uptake increases with temperature and hence the chemical phenomena (chemisorption) plays the main role in zinc adsorption on calcite surface. It was Zachara et al. [13–15] who analysed the chemisorption mechanism of zinc on calcite. It was stated from analysis of adsorption data that Zn^{2+} and $ZnOH^+$ were the sorbing species. Later authors specified by XPS, XRD and EDS methods that zinc can be precipitated in the form of zincite $Zn_5(OH)_6(CO_3)_2$.

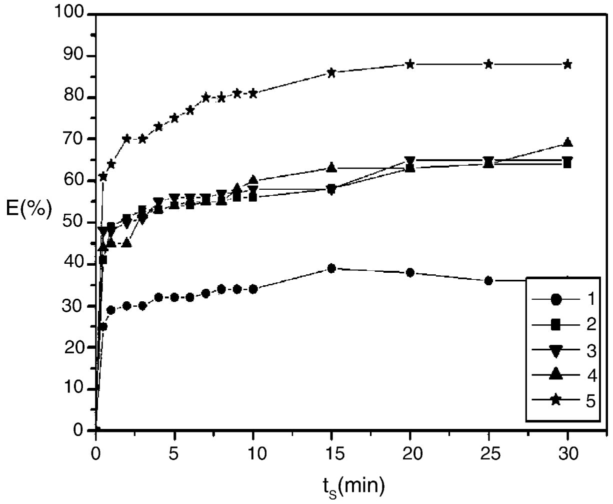

Fig. 5. Zinc uptake, E, vs. sorption time, t_S, for calcite milled in a planetary mill, temperature 25 °C, milling time: (1) 0 min, (2) 0.6 min, (3) 3 min, (4) 15 min and (5) 60 min.

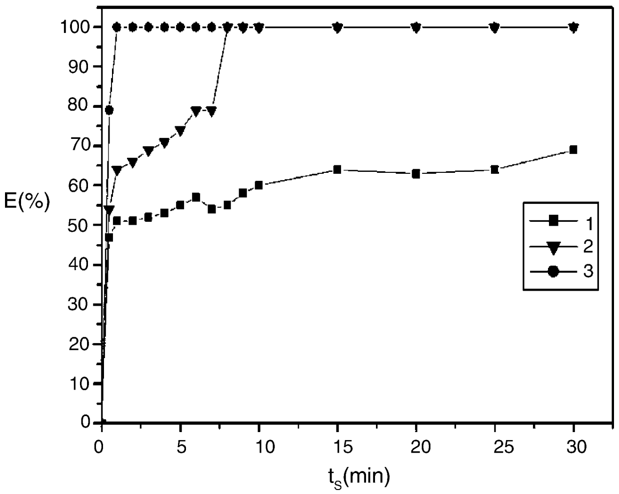

Fig. 6. Zinc uptake, E, vs. sorption time, t_S, for calcite milled in a planetary mill for 15 min, temperature: (1) 25 °C, (2) 35 °C and (3) 50 °C.

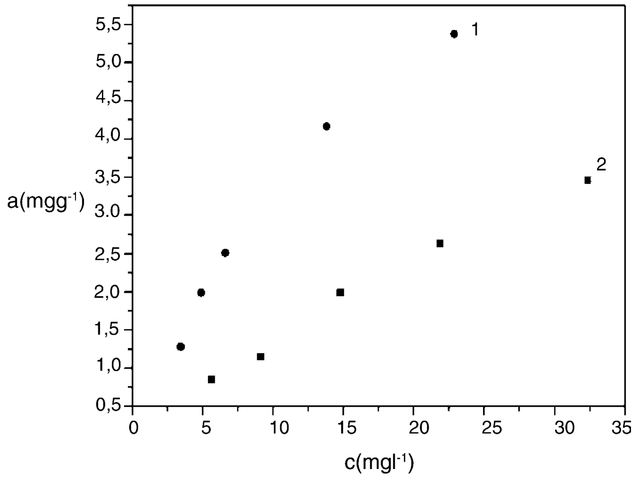

Fig. 8. Dependence of parameter a on parameter c of the Freundlich equation (3) for the zinc sorption onto calcite milled in a planetary mill (1) and calcite milled in vibratory mill (2), temperature 25 °C.

3.2.3. Effect of pH

The effect of pH on Zn sorption with calcite was examined. Initial pH of stock solution was 2. Alternating pH can also have a pronounced effect on metal–calcite interactions.

The extent of Zn sorption to calcite is pH dependent, with increased metal uptake as pH is increased [15], due to lower Ca^{2+} concentrations, and thus diminished competitive effects, which facilitate metal sorption. Changing pH can also affect metal aqueous speciation.

During sorption process pH increased from value 2 up to 7. This effect we can see in Fig. 7.

3.2.4. Adsorption isotherms

Equilibrium isotherms were obtained for zinc concentrations 10, 15, 25, 35 and 50 mg l^{-1}, respectively. Fig. 8 illustrates the application of the Freundlich equation (4) to the sorption of zinc onto both calcites. Fig. 9 shows that both isotherms fit the Freundlich model fairly well. This observation is consistent with conclusion that the Freundlich isotherm is generally valid for a broad range of a solute concentrations [31].

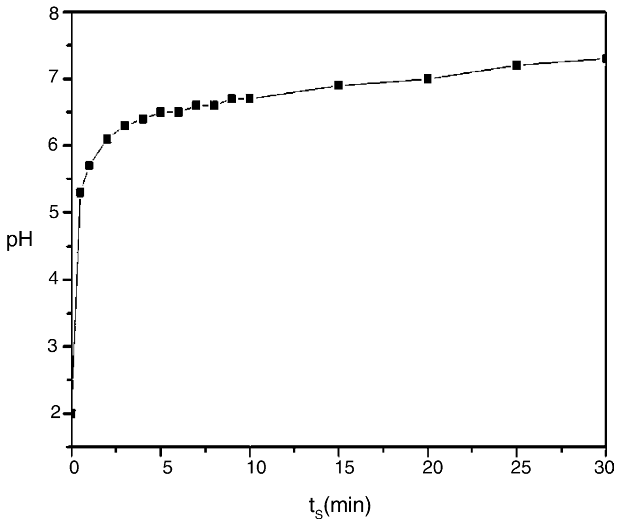

Fig. 7. Dependence of pH values on the sorption time, t_S, for calcite milled in a planetary mill.

3.2.5. Structure sensitivity of Freundlich equation constants

Freundlich [31] and Langmuir [35] models are widely used for study of adsorption processes till the present time. The Freundlich isotherm is an empiric formula with two parameters k and n, respectively. The main drawback for the isotherm is that the parameters have not exact meaning and have to be determined experimentally. However, recently a fundamental analysis of the isotherm for the adsorption of phenolic compounds on thermally activated carbon and correlation of its parameters with molecular properties of adsorbate and adsorbent have been performed [36]. The modified Freundlich parameter ($1/n$) was found to have an inverse linear relationships with the electron density of phenolics calculated from molecular orbital theory [37].

In this paper, the different approach has been applied. We have modified the solid-state properties of calcite by mechan-

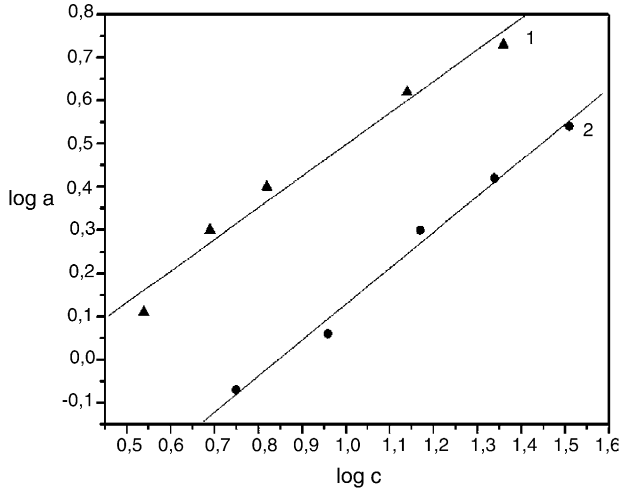

Fig. 9. Linearization of the Freundlich equation (4) for the sorption of zinc onto calcite milled in a planetary mill (1) and calcite milled in vibratory mill (2), temperature 25 °C.

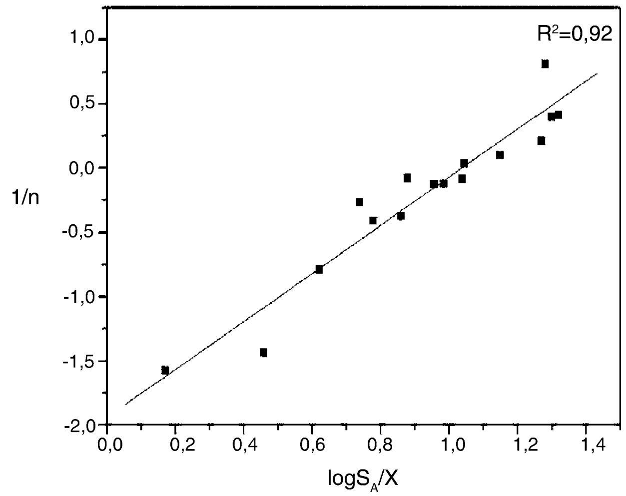

Fig. 10. Linear correlation between constant 1/*n* of Freundlich equation and logarithm of specific surface area and crystallinity ratio, S_A/X, calcite milled in a planetary mill.

ical activation and characterized it by the structure sensitivity parameter S_A/X (see Section 3.1.3). One solute (Zn^{2+}) was then applied for a series of mechanically activated calcites of different origin. The Freundlich parameter, 1/*n* was calculated from the linearization of adsorption isotherms and plotted against structure sensitivity parameter, $\log(S_A/X)$. The good linear correlation between 1/*n* versus $\log(S_A/X)$ values has been found (Fig. 10).

In the paper by Furuya et al. [37], Freundlich parameter (1/*n*) was related to the affinity between the adsorbate and the adsorbent. In our work, there is an evidence of relation of this parameter with the solid-state properties of adsorbent.

4. Conclusion

1. The mechanical activation of calcite by planetary and/or vibratory milling indicated its positive influence on the rate and efficiency of Zn uptake. This phenomenon is a consequence of increase in specific surface area S_A and decrease in crystallinity X of the milled samples.
2. Experiments with temperature changes proved the chemisorption plays the main role in zinc sorption on calcite.
3. The equilibrium isotherms of zinc sorption onto the mineral show the data correlate well with Freundlich model. The good linear correlation ($R = 0.92$) between Freundlich parameter 1/*n* and $\log(S_A/X)$ has been found.
4. The experimental results proved that the mechanically activated calcite is an effective sorbent for Zn removal from water solutions.

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References

[1] F. Habashi, A Textbook of Hydrometallurgy, Métallurgie Extractive Québec, Enr., Que., Canada, 1993.

[2] J.D. Hem, Chemistry and occurrence of cadmium and zinc in surface water and groundwater, Water Resour. Res. 8 (1972) 661–679.

[3] A.I. Zoubolis, K.A. Kydros, Arsenic(III) and arsenic(V) removal from solutions by pyrite fines, Sep. Sci. Technol. 28 (1993) 2449–2463.

[4] A. Mellah, S. Chegrouche, The removal of zinc from aqueous solutions by natural bentonite, Water Res. 31 (1997) 621–629.

[5] A. Garcia-Sanchez, E. Ayuso, O. Blas, Sorption of heavy metals from industrial waste water by low-cost mineral silicates, Clay Miner. 34 (1999) 469–477.

[6] T. Vengris, R. Binkiene, A. Sveikauskaite, Nickel, copper and zinc removal from waste water by a modified clay sorbent, Appl. Clay Sci. 18 (2001) 183–190.

[7] M. Prieto, P. Cubillas, A. Fernandez-Gonzales, Uptake of dissolved Cd by biogenic and abiogenic aragonite: a comparison with sorption onto calcite, Geochim. Cosmochim. Acta 67 (2003) 3859–3869.

[8] G.A. Sposito, The Surface Chemistry of Soils, Oxford University Press, Oxford, 1984.

[9] M.B. McBride, Chemisorption and precipitation of Mn^{2+} at the $CaCO_3$ surface, Soil Sci. Soc. Am. J. 43 (1979) 693–698.

[10] M.B. McBride, Chemisorption of Cd^{2+} on calcite surfaces, Soil Sci. Soc. Am. J. 44 (1980) 26–28.

[11] R.B. Lorens, Sr, Cd, Mn and Co distribution coefficients in calcite as a function of calcite precipitation rate, Geochim. Cosmochim. Acta 45 (1981) 553–561.

[12] P. Papadopoulos, D.L. Rowell, The reactions of copper and zinc with calcium carbonate surfaces, J. Soil Sci. 40 (1989) 39–48.

[13] J.M. Zachara, J.A. Kittrick, J.B. Harsch, The mechanism of Zn^{2+} adsorption on calcite, Geochim. Cosmochim. Acta 52 (1988) 2281–2291.

[14] J.M. Zachara, J.A. Kittrick, L.S. Dake, J.B. Harsch, Solubility and surface spectroscopy of zinc precipitates on calcite, Geochim. Cosmochim. Acta 55 (1989) 1549–1562.

[15] J.M. Zachara, C.E. Cowan, C.T. Resch, Sorption of divalent metals on calcite, Geochim. Cosmochim. Acta 55 (1991) 1549–1562.

[16] A. Aláčová, P. Baláž, Utilization of mechanically activated calcite ($CaCO_3$) for zinc sorption from solutions, Acta Metall. Slovaca 8 (2002) 241–246 (in Slovak).

[17] A. Garcia-Sanchez, E. Alvarez-Ayuso, Sorption of Zn, Cd and Cr on calcite. Application to purification of industrial wastewaters, Miner. Eng. 15 (2002) 539–547.

[18] R. Gómez del, P.J. Morando, D.S. Cicerone, Natural materials for treatment of industrial effluents: comparative study of the retention of Cd, Zn and Co by calcite and hydroxyapatite. Part I: batch experiments, J. Environ. Manage. 71 (2004) 169–177.

[19] T. Shahwan, B. Zünnbül, O. Tunusoglu, A.E. Eroglu, AAS, XRD, SEM/ESM and FTIR characterization of Zn^{2+} retention by calcite, calcite–kaolinite and calcite–clinoptilolite minerals, J. Colloid Interface Sci. 286 (2005) 471–478.

[20] P. Baláž, Extractive Metallurgy of Activated Minerals, Elsevier, Amsterdam, 2000, 290 pp.

[21] H. Zhang, R.L. Penn, R.J. Hammers, J.F. Banfield, Enhanced adsorption of molecules on surfaces on nanocrystalline particles, J. Phys. Chem. B 103 (1999) 4656–4662.

[22] H. Burns, M.A. Bredig, Transformation of calcite to aragonite by grinding, J. Chem. Phys. 25 (1956) 1281.

[23] J.M. Criado, J.M. Trillo, Effect of mechanical grinding on the texture and structure of calcium carbonate, J. Chem. Soc., Faraday Trans. 71 (1975) 961.

[24] R.B. Gammage, D.R. Glasson, The effect of grinding on the polymorphs of calcium carbonate, J. Colloid Interface Sci. 55 (1976) 396–401.

[25] G. Martinez, J. Morales, G. Munuera, Grinding induced transformations in $CaCO_3$, J. Colloid Interface Sci. 81 (1980) 500–506.

[26] Y. Iguchi, M. Senna, Mechanochemical polymorphic transformation and its stationary state between aragonite and calcite, Powder Technol. 43 (1985) 155–162.

[27] S. Jurečka, P. Šutta, A. Miškufová, T. Havlík, Study of $CaCO_3$ powder evolution at the milling in a vibratory mill, Mater. Struct. 10 (2003) 86–89.

[28] R. Schrader, B. Hoffmann, Changes in the reactivity of solids due to previous mechanical treatment, in: V.V. Boldyrev, K. Meyer (Eds.), Festkörperchemie, VED Deutscher Verlag für Grundstoffindustrie, Leipzig, 1973, pp. 522–543 (in German).

[29] T. Allen, Particle Size Measurement, Chapman and Hall, London, 1981, 250 pp.

[30] S.M. Ohlberg, D.W. Strickler, J. Am. Ceram. Soc. 45 (1962) 170–176.

[31] H. Freundlich, Űber die Adsorption in Lösungen, Z. Phys. Chem. 57 (1906) 385–470.

[32] F. Garcia, N. Le Bolay, C. Frances, Changes of surface and volume properties of calcite during a batch wet grinding process, Chem. Eng. J. 85 (2002) 177–187.

[33] M. Senna, Determination of effective surface area for the chemical reaction of fine particulate materials, Part. Part. Syst. Charact. 6 (1989) 163–167.

[34] K. Tkáčová, P. Baláž, Structural and temperature sensitivity of leaching of chalcopyrite with iron(III) sulphate, Hydrometallurgy 21 (1988) 103–112.

[35] I. Langmuir, The adsorption of gases on plane surface of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[36] Y. Otake, N. Kalili, T.H. Chang, E. Furuya, Relationship between Freundlich type equation constants and molecular orbital properties, in: Proceedings of the Annual Meeting AICHE, Reno, Nevada, Poster 712, 2001.

[37] E.G. Furuya, H.T. Chang, Y. Miura, K.E. Noll, A fundamental analysis of the isotherm for the adsorption of phenolic compounds on activated carbon, Sep. Purif. Technol. 11 (1997) 69–78.