

A Novel Sorbents of Metal Ions Based on Thermally Activated, Acidic and Non-acidic Treated Dolomite

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Abstract The development of a novel sorbents for the removal of toxic metal ions from wastewaters is an important task for the research community. In this study, the different approaches of physical-chemical modification (thermal activation, acidic and non-acidic treatment) of natural dolomite were proposed in order to synthesize highly effective sorption materials. The effect of dolomite modification conditions on sorption properties of prepared sorbents was studied. It was shown that these sorbents could find practical applications for the sorptive purification of mine water from metal ions.

Key words sorption, metal ions, mine water, waste water, dolomite

Introduction

At near future the principals of green chemistry and zero waste technologies will be in the focus of industrial and mining enterprises. So, the development of a novel sorbents for the removal of toxic metal ions from wastewaters is an important task for the research community (Fu 2010). Natural materials (zeolites and clays, phosphate rocks and carbonate-containing minerals) are attractive candidates for the development of highly effective sorbents for metal ions. It is well known that in a native form these materials have a low effectiveness and do not fit for the practical use (Babel 2003).

Recently, the different approaches of physical-chemical modification (thermal activation, acidic and non-acidic treatment) of natural dolomite were proposed in order to synthesize highly effective sorption materials. The aim of this work was to study the effect of dolomite modification conditions on sorption properties of prepared sorbents towards metal ions.

Methods

Preparation of sorbents and solutions

Dolomite from the Ruba deposit with the following chemical composition (in wt %): SiO₂ 1.1, Fe₂O₃ 0.4, Al₂O₃ 0.5, CaO 30.3, MgO 20.0, SO₃ 0.4, K₂O 0.2, Na₂O 0.1 and calcination loss 47.0 was used. The heat treatment of the samples was performed in a SNOL 7.2/1300 electrical resistance furnace in the temperature range of 700–900 °C, with keeping at the final temperature for 5 h. The heating rate was fixed at 5 °C/min. For the synthesis of sorbent with a high content of calcium and magnesium phosphates and high sorption properties, it was previously suggested to activate the natural dolomite by calcination at 800 °C.

The sorbent PD-1 was obtained after 24 h of stirring dolomite with 20% phosphoric acid at a dolomite to phosphoric acid weight ratio of 1 : 3. To prepare the sorbent PD-2, activated dolomite was dissolved in concentrated nitric acid, and thereafter Ca and Mg phosphates were precipitated at pH 10 using ammonium phosphate. Details can be found elsewhere. In contrast to previous work, the synthesis was conducted by slow controlled titration ($5 \text{ mL}\cdot\text{s}^{-1}$), and, after total addition of the ammonium phosphate solution, the suspension was created within 24 h. After aging and washing with distilled water, the precipitate of Ca-Mg phosphate was rinsed with ethanol. Replacement of intermicellar liquid (water with ethanol) yields a sorbent with a more developed mesoporous structure, because ethanol has a lower surface tension than water. By this means, sorbent PD-1 represents a mixture of Ca-Mg hydrogen phosphates with the approximate composition $(\text{Mg,Ca})\text{HPO}_4 \cdot x\text{H}_2\text{O}$. PD-2 represents a mixture of Ca-Mg tertiary phosphates with the total formula $(\text{Mg,Ca})_3(\text{PO}_4)_2 \cdot y\text{H}_2\text{O}$.

Sample PD-3 was obtained using soft non-acid method, after 16 h of stirring dolomite with $0.2 \text{ M NaH}_2\text{PO}_4$ at a dolomite to NaH_2PO_4 ratio of 1.4 : 33 $\text{g}\cdot\text{mL}^{-1}$. Theoretical calculations suggest that this quantity is enough for full interaction between magnesium oxide and sodium phosphates.

Aqueous solutions of M(II) ions were prepared by dissolving a weighed mass of analytical grade salts $\text{M}(\text{NO}_3)_2$ (Sigma-Aldrich). Strong HCl or HNO_3 acids were used for washing out the laboratory glassware. Distilled water was used for all experiments.

Analytical methods

XRD patterns were collected on an ADVANCED D8 powder diffractometer (CuK_α radiation, $2\theta = 10\text{--}60$ deg., Bruker, Germany). Phase identification of the samples was carried out using XRD standard base JCPDS PDF2. The file number is shown in brackets in the figure captions. Low temperature (77 K) nitrogen physisorption–desorption was studied by a static volume method using a surface/porosity analyzer (Micromeritics ASAP 2020 MP, USA).

For elemental composition analysis, the sorbents were dissolved in 6 M nitric acid. Total calcium and magnesium concentration was determined using complexometric EDTA titration, while magnesium concentration was determined using an atomic-absorption technique. The concentration of PO_4^{3-} was defined spectrophotometrically as phosphovanadomolybdate complex at $\lambda = 440 \text{ nm}$.

The concentration of M(II) ions present in the model solutions in the course of the sorption experiments was measured using an atomic absorption spectrometer (Contr AAS 300, Analytic Jena, Germany).

Sorption study

The adsorption capacity was calculated using the following equation:

$$q_t = (C_0 - C_t) \frac{V}{m} \quad (1)$$

where C_0 and C_t ($\text{mmol}\cdot\text{L}^{-1}$) are the initial concentration and the concentration of M(II) at contact time t (min), V (L) is the solution volume and m (g) is the sorbent mass.

The influence of initial concentration of M(II) solutions on the sorption capacity of the synthesized sorbents was determined by varying metal concentration in the range from 0.5 to 25 $\text{mmol}\cdot\text{L}^{-1}$. For this study, 0.2 g of a sorbent was mixed with 50 mL of model solution at room temperature for the contact time of 24 h. The data obtained in these experiments were used to create sorption isotherms and these were fitted to the Langmuir, Freundlich, Redlich-Peterson and Sips isotherm models, which are most often used to describe the adsorption of one component (Foo 2010).

For dynamic sorption in case of PD-3 the multicomponent aqueous solution of Pb^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Ni^{2+} , Sr^{2+} and Co^{2+} ions was prepared by dissolving nitrate salts in distilled water at a concentration of 5.0 $\text{mg}\cdot\text{L}^{-1}$ of each metal. The sorption experiments were carried out in dynamic mode. Sorbents were placed in glass column with diameter 1.0 cm, the height of sorbent was 5.0 cm. The linear rate of filtration was 10 $\text{m}\cdot\text{h}^{-1}$ (the contact time was 47 ± 3 sec.).

The removal efficiency was calculated using the following equation:

$$\alpha = \frac{\tilde{N}_0 - \tilde{N}_a}{\tilde{N}_0} \times 100\% \quad (2)$$

where α is removal efficiency in %, C_0 and C_e are concentration before and after sorption, $\text{mg}\cdot\text{L}^{-1}$.

Results and discussion

Characterization of sorbents

Samples of natural dolomite D-700, D-800, and D-900 thermally activated at 700, 800, and 900°C, respectively were tested as sorbents. According XRD data, the sample D-700 is complex in composition containing both the original dolomite and calcium carbonate doped with magnesium oxide. The D-800 sample contains predominantly calcium carbonate and magnesium oxide, while D-900 sample is a mixture of calcium and magnesium oxides with a small calcium carbonate admixture.

According to the XRD data (fig. 1) and chemical analysis (Table 1), the PD-1 sample is a mixture of calcium and magnesium hydrogen phosphates with the gross composition $\text{Ca}_2\text{Mg}(\text{HPO}_4)_3 \cdot 8.7\text{H}_2\text{O}$. Sorbent PD-2 is composed of calcium, magnesium and magnesium-ammonium secondary phosphates, and can be described by the formula $\text{CaMg}_{1.5}(\text{NH}_4)(\text{PO}_4)_2 \cdot 12.5\text{H}_2\text{O}$. PD-3 is a mixture of calcium and magnesium tertiary and hydrogen phosphates, calcium carbonate and magnesium oxide, with the composition $\text{Ca}_{0.6}\text{Mg}_x(\text{PO}_4)_y(\text{HPO}_4)_{1.6-y}(\text{CaCO}_3)_{4.7}(\text{MgO})_{5.1-x} \cdot 7.8\text{H}_2\text{O}$. Due to the fact that calcium and magnesium tertiary phosphates obtained by precipitation are amorphous compounds, their reflexes are absent from the diffraction pattern of the PD-2 sorbent. In contrast, magnesium-ammonium phosphate is characterized by a high degree of crystallinity, which is confirmed by clearly visible reflexes.

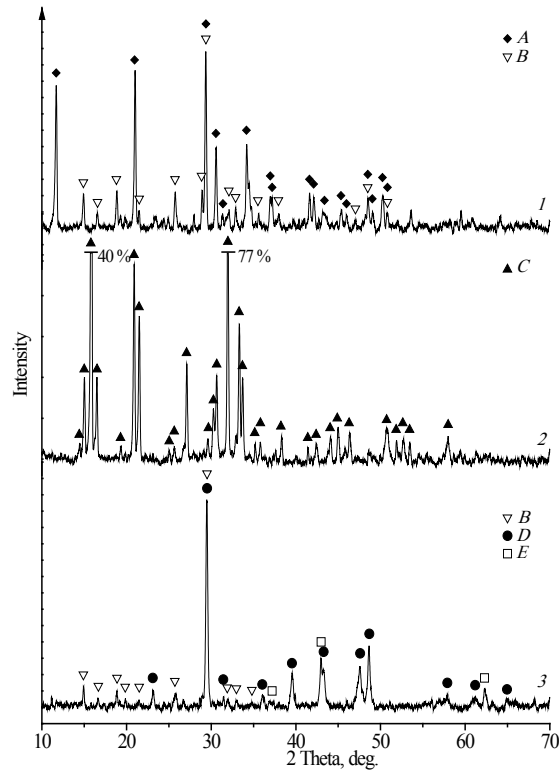


Figure 1 XRD patterns of PD-1 (1), PD-2 (2) and PD-3 (3) (A – $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ [9-77], B – $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ [35-780], C – $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ [71-2089], D – CaCO_3 [5-586], E – MgO [78-430]).

Table 1 Chemical composition of Ca-Mg phosphate sorbents.

Sorbent	Ca	Mg	Content, mmol·g ⁻¹				Ca/Mg	(Ca+Mg)/P
			NH ₄	CO ₃	PO ₄	H ₂ O		
PD-1	3.91	1.99	-	-	4.93	17.39	1.96	1.20
PD-2	1.84	3.07	1.52	-	3.78	23.70	0.60	1.50
PD-3	5.27	5.09	-	4.65	1.56	7.78	1.04	6.65

Table 2 shows the differences in the porous structure parameters of the obtained sorbents. The highest specific surface area was obtained for PD-2: A_{sp} 49 and A_{BET} 54 m²·g⁻¹. For samples PD-1 and PD-3, the values were about 15–20 m²·g⁻¹. The PD-2 sample had the highest pore volume, 0.182–0.238 cm³·g⁻¹, which was about 3–4 times higher than for the other two sorbents. The data distribution of the average pore sizes indicated that the PD-3 samples had the smallest pore size, about 11–12 nm.

Table 2 Adsorption and textural properties of Ca-Mg phosphate sorbents.

Sample	Surface area, m ² ·g ⁻¹		Pore volume, cm ³ ·g ⁻¹		Pore size, nm	
	Single point	BET	Ads.	Des.	Ads.	Des.
PD-1	19	22	0.069	0.080	14	16
PD-2	49	54	0.182	0.238	15	19
PD-3	15	17	0,041	0,043	11	12

When NaH₂PO₄ was used as a phosphating reagent the main product was magnesium hydrophosphate trihydrate, MgHPO₄·3H₂O, and its peaks appeared only after 24 h of interaction (figs. 2, a-c). The relative intensities of calcium carbonate and magnesium oxide reflexes altered slightly during contact with Na₂HPO₄ solution. The relative intensity of the magnesium oxide reflexes decreased, indirectly suggesting that phosphate is formed in the interaction with the magnesium oxide on the surface of the granules. The lack of appropriate phases of magnesium phosphate may be due to their relatively low content and low crystallinity. The sample obtained after 16 h was used as sorbent PD-3.

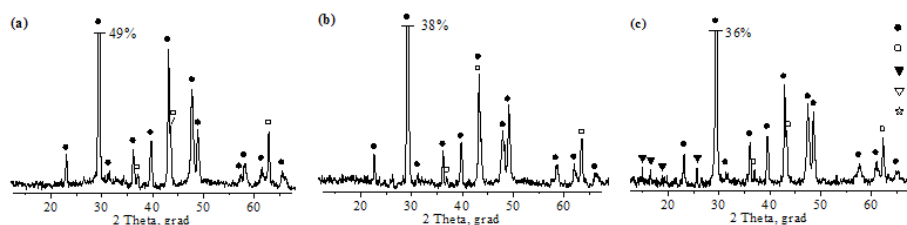


Figure 2 XRD patterns of granular dolomite after contact with 0.2 M solutions of NaH₂PO₄ during (a) 2, 8 (b) and 24 h (c) (1 – CaCO₃; 2 – MgO; 3 – MgHPO₄·3H₂O; 4 – MgCa₂(PO₄)₂·2H₂O; 5 – CaO).

Sorption of metal ions

At the equilibrium concentration of Co²⁺ ions 50-60 mg·L⁻¹, all sorption isotherms of thermally activated dolomite out on a plateau, this indicates the reaching of maximum sorption capacity of the studied sorbents (fig. 3). The increase of temperature from 700 to 900 °C causes a significant increase in the sorption capacity of dolomite from 8 to 500 mg·g⁻¹. The behaviour of the thermally activated dolomite in sorption processes depends on their composition and different chemical properties. Sorbent D-700 has weakly basic properties, pH of aqueous extract for it is 11.4. The sorbents D-800, D-900, containing more of magnesium oxide, and calcium oxide (D-900) – materials with more basic properties, pH value of the aqueous extract for the D-800 and D-900 are 12.5 and 12.9, respectively. It is known that the deposition of Co(OH)₂ begins at pH of 6.6 and 7.6, and ends at a pH of 9.2. So, it can be assumed that the samples D-800 and D-900 operates mainly function of “precipitator”. This is confirmed by the XRD results, according to which the main reaction product D-700 with an aqueous solution of Co(NO₃)₂ is a basic cobalt carbonate Co(CO₃)_{0.5}(OH)·0.11H₂O, and in the case of D-800, D-900 – cobalt hydroxide Co(OH)₂.

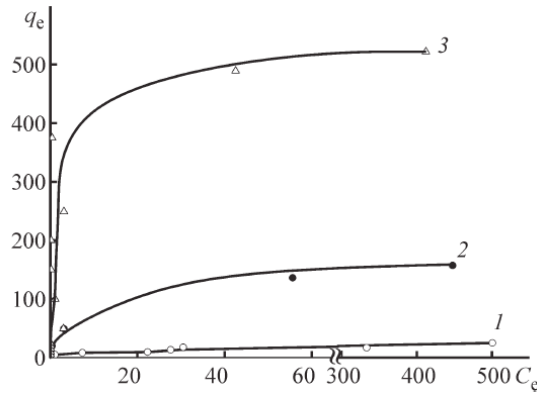


Figure 3 Sorption isotherms of Co^{2+} by (1) D-700, (2) D-800, (3) D-900 (q_e , $\text{mg}\cdot\text{g}^{-1}$, C_e , $\text{mg}\cdot\text{L}^{-1}$).

The isotherms of sorption of Ni^{2+} , Co^{2+} , Cu^{2+} and Zn^{2+} ions by sample PD-1 from single-component solutions can be attributed to the type L, according to the classification of Giles, and only the isotherm sorption of Ni^{2+} has the asymptotic plateau. This suggests that the maximum sorption capacity of the sorbent is not achieved (fig. 4, a). However, such a course of the isotherms can be obtained as a result of addition of two Langmuir isotherms. Isotherm sorption of Pb^{2+} is characterized by an initial vertical section and is of type H used to describe the sorption of substances with very high affinity to the sorbent. In contrast to the above form of isotherms sorption isotherms of Cd^{2+} has a complex – sigmoid form (type S). Adsorption isotherms were built for each tested metal ions and were found to fit to Freundlich and Redlich-Peterson models. The sorbent PD-1 is characterized by high sorption capacity in relation to ions of Zn^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Ni^{2+} and Co^{2+} (1.19–3.78 $\text{mmol}\cdot\text{g}^{-1}$).

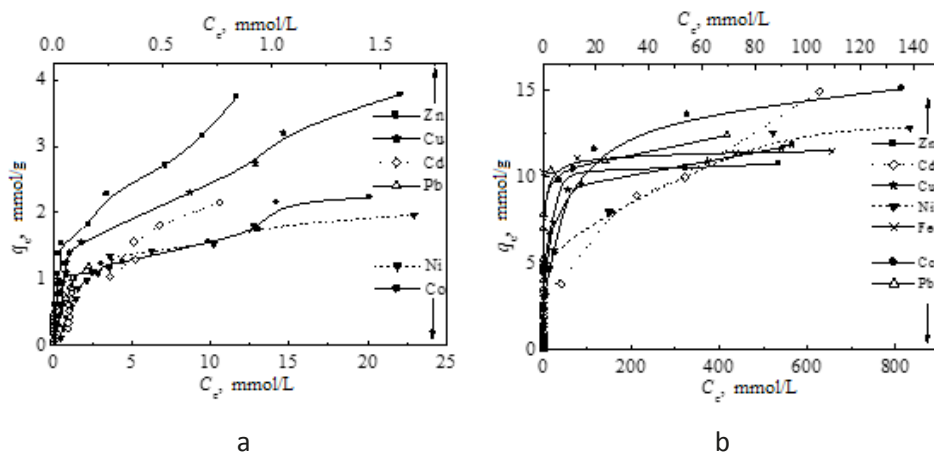


Figure 4 Sorption isotherms of metal ions by PD-1 and PD-2 samples.

Sorption isotherms of Zn^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Ni^{2+} and Co^{2+} ions by sample PD-2 can be attributed to the H-type (fig. 4, b). This is the case when the adsorption is so effective that in dilute solutions the residual concentration of trace metals and is hard to define. Adsorption activity in relation to ions of metals increases with their ionic radius. Experimental data can be described more precisely with Redlich-Peterson model for Zn^{2+} , Cu^{2+} , Ni^{2+} and Co^{2+} . The complexity of choosing models for cadmium Cd^{2+} , Fe^{2+} and Pb^{2+} sorption by synthesized sorbent arises due to the complex mechanism of sorption. Among all tested metals, highest adsorption capacity of PD-2 was detected towards Co^{2+} and Pb^{2+} (15 and 12 $\text{mmol}\cdot\text{g}^{-1}$, respectively) and the lowest towards Zn^{2+} , Fe^{2+} and Cu^{2+} (about 8 $\text{mmol}\cdot\text{g}^{-1}$).

Analysis of dynamic sorption curves (fig. 5) shows that the sorbent PD-3 the removal efficiency for all ions except Ni^{2+} and Co^{2+} was 80-95 % when treating over 200 ml of the model solution. The maximum removal efficiency (about 95%) was observed for Zn^{2+} . High removal efficiency was also observed towards Cd^{2+} and Sr^{2+} (85-90%), while somewhat lower removal efficiency was observed for Pb^{2+} and Cu^{2+} (70-80%). The removal efficiency curves for Ni^{2+} and Co^{2+} were distinctive; the removal efficiency of Co^{2+} was about 40%, and for Ni^{2+} it did not exceed 20%. It is important to note that the removal efficiency values for all the studied metal ions persisted in the whole studied range of volumes of the cleaned solution. The affinity of this sorbent towards metal ions could be arranged as follows: $\text{Zn}^{2+} > (\text{Cd}^{2+} \approx \text{Sr}^{2+}) > (\text{Cu}^{2+} \approx \text{Pb}^{2+}) > \text{Ni}^{2+} > \text{Co}^{2+}$.

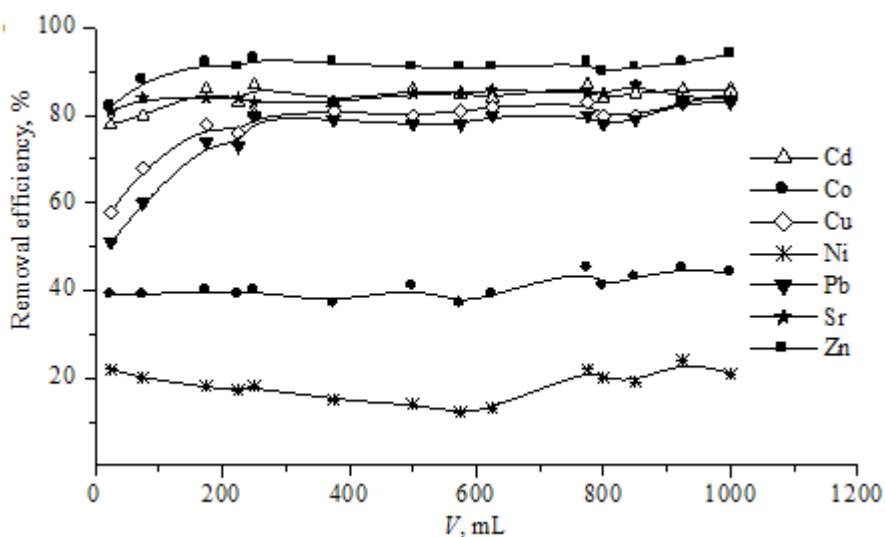


Figure 5 Evolution of removal efficiency depends on the volume of treated solution by sorbent PD-3.

Conclusions

A novel sorbents of metal ions based on thermally activated, acidic and non-acidic treated dolomite were obtained. The sorption properties towards toxic metal ions in batch experiment and dynamic mode were studied. The main advantages of sorbents based on modified

dolomite are high sorption capacity and kinetic parameters, low cost and possibility for the re-use of utilized sorbents, e.g. as a pigment for production of building materials. It indicates that these sorbents could find practical applications for the sorptive purification of mine water from metal ions.

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References

- S. Babel, T.A. Kurniawan (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review, *J. Hazard. Mater.* 97: 219–243, doi:10.1016/S0304-3894(02)00263-7
- K.Y. Foo, B.H. Hameed (2010) Insights into the modeling of adsorption isotherm systems, *Chem. Eng. J.* 156: 2–10, doi: 10.1016/j.cej.2009.09.013
- F. Fu, Qi Wang (2011) Removal of heavy metal ions from wastewaters: A review, *J. Environ. Manag.* 92: 407–418, doi: 10.1016/j.jenvman.2010.11.011