Periodica Polytechnica
Chemical Engineering

61(1), pp. 27-32, 2017
DOI: 10.3311/PPch.9871

RESEARCH ARTICLE

Use of La-, Ce-, Y-, Fe- bentonites for Removing Phosphate Ions from Aqueous Media

Dóra Buzetzky[1*], Noémi M. Nagy[1], József Kónya[1]

Received 08 August 2016; accepted after revision 13 December 2016

Abstract
Clays play an important role in the environment. By removing cations and anions either through ion exchange, adsorption and precipitation, or all these combined, they can act as natural decontaminating agents of numerous pollutants. In this study, four modified bentonites (La-, Ce-, Y-, Fe-bentonite) were prepared and characterized, and their phosphate sorption capabilities were measured in batch experiments. Equilibrium times were also examined. The activation energy of the sorption process was calculated. The La- , Ce- and Y-bentonite can bind similar amount of phosphate ions, while iron-bentonite can bind only half of it compared to La-, Ce- and Y-bentonite.

Keywords
modified bentonite, phosphate sorption, eutrophication, phosphate sorption kinetics

1 Introduction

Phosphorus is one of the main mineral nutrients, thus it is an essential and important element for all natural organisms, including algae. However, high concentration of phosphate in natural waters (over 0.03 mg/dm^3) may lead to eutrophication, which is considered as one of the most important water quality problems today. The eutrophication may cause a series of problems, for example: reducing light transmission, decreasing biodiversity, and generating algal blooms [1, 2, 3].

Phosphates may originate from agricultural fertilizers, treated and untreated sewage, organic matter, soaps and detergents and from diffuse sources (urban water runoff) or from natural sources (solubilization of rocks) [4, 5]. Natural sediments and pure minerals have recently drawn attention for their remarkable success of removing the dissolved phosphates through sorption processes. Nowadays there is growing interest in finding inexpensive and effective clays as phosphate sorbents from natural water bodies. The sorption of phosphate, nitrate, arsenate etc. anions on clays, is the result of electrostatic attraction and ligand exchange [6].

Bentonite is a low cost and readily available clay, which is getting more widely used for environmental-oriented applications [7].

Several studies have been carried out on sorption of phosphates. Solid-phase phosphate sorbents are mainly clays enriched with aluminum (Al) [8], iron (Fe) [9] or lanthanum (La) [10], aluminum oxide [11], hydroxide sludge [12], ferrihydrite [13], oxide tailings [14], titanium dioxide [15] and zeolite [16].

Montmorillonite is the main clay mineral of bentonite, which can be used as a model substance in the study of the interfacial processes of rocks and soils. It is a layer silicate, a member of the smectite group. It has many agricultural, industrial, and environmental applications [17]. It consists mostly of calcium montmorillonite, with permanent negative charges on its surface. Bentonite can intercalate inorganic and/or organic cations and the materials resulted have high specific surface area. Cation exchange capacity of bentonite makes it especially appropriate to describe the interface processes and examination of sorption phenomena [18]. In modified bentonites the

[1] Imre lajos Isotope Laboratory,
Department of Physical Chemistry,
University of Debrecen
Debrecen, Egyetem tér 1, 4032, Hungary
[*] Corresponding author, e-mail: buzetzkyd@gmail.com

interlayer cations are participating in the cation exchange process (e.g. Na^+, K^+, Ca^{2+}, Mg^{2+}) [17].

Many information exists about La- modified bentonite Phoslock, invented by CSIRO (Commonwealth Scientific and Industrial Research Institution) in Australia in the mid-1990s [10]. Beside the La-modified bentonite, more economical alternatives, such as yttrium (III), cerium (III) and iron (III) ions modified bentonites were also investigated.

2 Materials and methods

2.1 Preparation of modified bentonites

Bentonite was collected in Istenmezeje, Hungary. Elemental analysis of the original Ca-bentonite (measured with EDAX) resulted in the following composition: 73.29 % SiO_2, 18.71 % Al_2O_3, 1.48 % Fe-oxide, 2.29 % CaO and 4.23 % MgO [19]. X-ray diffraction and thermoanalytical data show 71 m/m% montmorillonite content. The other constituents were: 12 m/m% kristobalite/ opal CT, 8 m/m% illite, 4 m/m% quartz, 3 m/m% kaolinite and 2 m/m% calcite. During X-ray diffraction the samples were measured by a Philips PW1710 powder diffractometer equipped with a CuK_α source and a graphite monochromator (operating at 30mA, 40kV). The scan rate was 2°2Θ/min.

The cation exchange capacity (CEC) was determined by ammonium acetate method [20]. The CEC value of Ca-bentonite is 81 meqv/100g.

Rare earth (REE) bentonites were prepared by an ion exchange process using bentonite and rare-earth solution. Ca^{2+} bentonite (20 g) was suspended in $REEClO_4$ solutions ($4.7x10^{-2}$ mol/dm^3). The solutions were shaken for 5 hours, then centrifuged, washed, and dried at room temperature. $REEClO_4$ were prepared by dissolving REE oxides (purchased from Johnson, Matthey & Co., pro anal, with no Fe content (checked)) in 37 W/W% HCl) [19].

For iron (III)-bentonite, $FeCl_3$ (50 g) was solved in acetone while cooling bath was used because of significant solvation heat. After the whole of $FeCl_3$ was dissolved, and a stoichiometric amount of Ca-bentonite (based on calcium and iron (III) ions) was added to the system. The product was placed on a magnetic stirrer for 1 hour, in order to facilitate homogenization and it was filtered. Then the bentonite was washed with acetone and air dried at room temperature [21].

The elemental composition of the adsorbents was determined by X-ray fluorescence spectroscopy (XRF). Instrumental parameters were:

1. Si(Li) detector with 20 mm^2 surface and 3.5 mm evaporated layer (Atomki, Debrecen, Hungary),
2. Canberra DSA 1000 digital spectrum analyzer (Canberra Industries, Meriden, CT 06450, USA),
3. Canberra Genie 2000 3.0 spectroscopy software (Camberra Industries, Meriden, CT 06450, USA).

The K_α-lines of the lanthanide elements can be excited with 185 MBq ^{241}Am radioactive source.

2.2 Kinetic studies of phosphate on modified bentonites

Phosphate sorption experiments were conducted using a batch technique. The modified bentonite (100 mg) was added to 20 cm^3 of KH_2PO_4 ($5x10^{-4}$ mol/dm^3). During this measurement the rate of sorption of phosphate ion was measured on La(III)-, Ce(III)-, Y(III)- and Fe(III)- bentonite after 10-300 min shaking. All samples were placed in a Bühler KS15A shaking bath at the desired temperature (1, 25, 40 °C). For cerium and yttrium the soprtion was faster, so the reaction time was at 2-120 min. After the sorption samples were filtered through a 0.45 µm pore size syringe filter, the concentration in the supernatant (c_e) was measured by the molybdate blue spectrophotometric method using a Cary 100 UV-VIS spectrophotometer at 660 nm [22]. pH was measured with Clean PH200 pH meter, and Clean Cs1030 combined glass electrode. The amount of the sorbed phosphate was calculated in the following way: the difference of the initial and the measured phosphate concentration (after the given time) was divided by the amount of bentonite sorbent. In addition to the photometric measurements, the kinetics of the phosphate sorption was calculated using the software called Scientist. The first-order kinetic model Eq. (1) is:

$$A = A_e * \left(1 - \exp\left(-kt\right)\right) \tag{1}$$

where t is the time, A is the phosphate concentration in bentonite at any time, A_e is the maximum amount of sorbed phosphate on bentonite, k is the first-order rate constant.

2.3 Equilibrium studies of phosphate on modified bentonites

The sorption isotherms were determined by batch equilibration of 100 mg of each bentonite sample with 20 cm^3 of aqueous phosphate solutions of varied initial concentrations (ranging from 0.005 to 0.0005 mol/dm^3). All samples were placed in a Bühler KS15A shaking bath at the desired temperature. In order to determine the effect of temperature on sorption, isotherms were established at 1, 25, 40 °C. After the equilibrium time (1h) defined in the kinetic experiments the samples were filtered through a 0.45 µm pore size syringe filter and then the concentration in the supernatant (c_e) was measured with spectrophotometer. The amount of the sorbed phosphate was calculated in the following way: the difference of the initial and the measured phosphate concentration (after the given time) was divided by the amount of bentonite sorbent (a_e). The Langmuir equation (2) is commonly used to describe phosphate equilibrium sorption on soils, phyllosilicate minerals and metal oxides, and can be expressed mathematically as follows:

$$\frac{c_e}{a_e} = \frac{c_e}{z} + \frac{1}{zK} \tag{2}$$

Where a_e is the amount adsorbed at equilibrium (mol/g), c_e is the equilibrium solution concentration (mg/l), z is the maximum sorption capacity (mg/g) and K is solubility [17].

2.4 Desorption experiments of phosphate on modified bentonites

These experiments aimed to determine the quantity of phosphate which can undergo desorption. The modified bentonite (100 mg) was added to 20 cm^3 of KH_2PO_4 (5x10^{-4} mol/dm^3). The samples were placed in a Bühler KS15A shaking bath at 25 °C. After the sorption samples were filtered through a 0.45 µm filter and then the concentration in the supernatant (c_e) was measured by the molybdate blue spectrophotometric method using a Cary 100 UV-VIS spectrophotometer at 660 nm. The modified bentonites saturated with phosphate (100 mg) were added to 20 cm^3 of distilled water. All samples were placed in a Bühler KS15A shaking bath at 25 °C. After the equilibrium time the samples were filtered through a 0.45 µm pore size syringe filter and then c_e was measured with spectrophotometer.

3 Results and discussion

3.1 Results of XRF measurements

Table 1 La, Ce, Y, and Fe concentrations of bentonite measured by X-ray fluorescence analysis (XRF)

	La-bentonite	Ce-bentonite	Y-bentonite	Fe-bentonite
XRF (mol/g)	3.50E-04	2.92E-04	3.50E-04	4.85E-04
CEC % (REE content related to CEC)	130	108	130	179

REE and Fe concentrations measured by X-ray fluorescence analysis are summerized in Table 1. The REE content is given in mol/g. The bounded REE's are given in percentage compared to CEC. This means that the REE concentration was higher than expected from CEC.

3.2 Sorption kinetics of phosphate on modified bentonites

The sorption kinetic data of phosphate on the four bentonites are presented as a function of contact times (Figs. 1-4). The sorption of phosphate on the four bentonites increases with time.

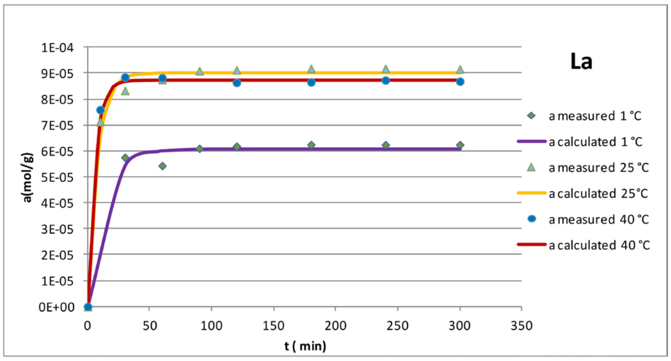

Fig. 1 Phosphate sorption kinetics at 1 °C, 25°C, and 40°C on lanthanum modified bentonite, 100 mg bentonite, 20 cm^3 5x10^{-4} mol/dm^3 KH_2PO_4, pH 4.4- 5.2

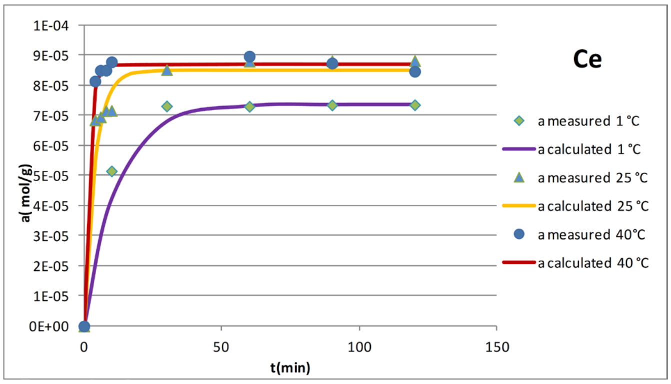

Fig. 2 Phosphate sorption kinetics at 1 °C, 25 °C, and 40°C on cerium modified bentonite 100 mg bentonite, 20 cm^3 5x10^{-4} mol/dm^3 KH_2PO_4, pH 6.1-8

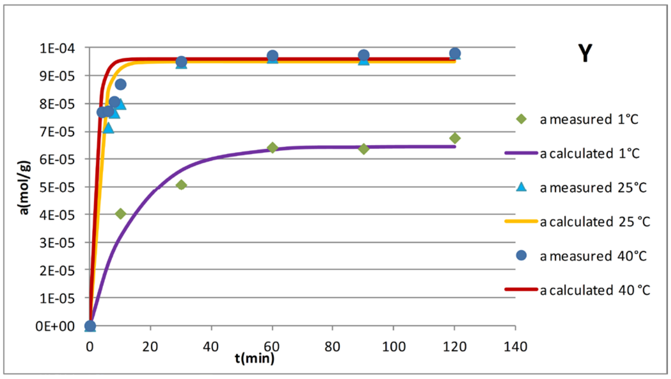

Fig. 3 Phosphate sorption kinetics at 1 °C, 25 °C, and 40°C on yttrium modified bentonite 100 mg bentonite, 20 cm^3 5x10^{-4} mol/dm^3 KH_2PO_4, pH 4.1-5

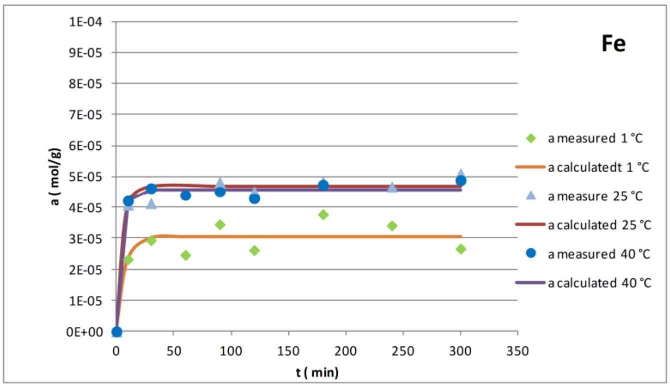

Fig. 4 Phosphate sorption kinetics at 1 °C, 25 °C, and 40°C on iron modified bentonite 100 mg bentonite, 20 cm^3 5x10^{-4} mol/dm^3 KH_2PO_4, pH 3.2-3.5

Table 2 Kinetic parameters at different temperatures and E_a values on La- and Ce modified bentonite **(A_e and k was calculated from the Eq. (1).)**

La-bentonite			**Ce-bentonite**		
E_a	22	kJ/mol	**E_a**	27	kJ/mol
***1* °C**			***1* °C**		
A_e	7.1E-05	mol/g	A_e	7.4E-05	mol/g
k	0.05	1/min	k	0.10	1/min
pH	4.5-4.6		pH	6.3-6.8	
***1* °C**			***1* °C**		
A_e	7.71E-05	mol/g	A_e	7.4E-05	mol/g
k	0.052	1/min	k	0.34	1/min
25 °C			**25 °C**		
A_e	8.9E-05	mol/g	A_e	8.5E-05	mol/g
k	0.15	1/min	k	0.31	1/min
pH	4.4-4.7		pH	6.1- 8	
			25°C		
			A_e	8.3E-05	mol/g
			k	0.49	1/min
40 °C			**40 °C**		
A_e	8.7E-05	mol/g	A_e	8.7E-05	mol/g
k	0.20	1/min	k	0.67	1/min
pH	4.8-5.2		pH	6.2-7	
			40 °C		
			A_e	8.86E-05	mol/g
			k	0.68	1/min

In order to estimate the activation energy (*Ea*) of the phosphate sorption, the kinetic data were analyzed by the Arrhenius equation (3). The activation energy (*Ea*) was calculated from the slope of the ln (*k*) versus 1/T plots.

$$\ln(k) = \ln(k_o) - \frac{Ea}{RT} \tag{3}$$

where E_a is the activation energy (kJ/mol), *R* is the gas constant (8.314 J/K mol), *T* is the temperature (*K*), and k_0 is Arrhenius constant [23].

The calculated Ea values are presented in Table 2 and in Table 3, which show that these values were higher than the corresponding value for other adsorbents. For example, Ea value for the adsorption of phosphate onto dolomite is 5.44 kJ/mol [24]. Similar E_a results were obtained for La-bentonite, according to Hagseresht [10] the E_a value was higher than expected. In our opinion, these activation energy values cannot be too high because the typical range of the diffusion activation energy of heterogeneous reaction is in the range of 8-33 kJ/mol. The diffusion of the relatively large phosphate ion in the interlayer space of montmorillonite is thought to be the rate determining step.

Table 3 Kinetic parameters at different temperatures and Ea values on Y- and Fe modified bentonite **(A_e and k was calculated from the Eq. (1).)**

Y-bentonite			**Fe-bentonite**		
Ea	37	kJ/mol	**Ea**	10	kJ/mol
***1* °C**			***1* °C**		
A_e	6.4E-05	mol/g	A_e	3.11E-05	mol/g
k	0.08	1/min	k	0.14	1/min
pH	4.2-4.9		pH	3.2	
			30 °C		
			A_e	4.7E-05	mol/g
			k	0.19	1/min
			pH	3.2-3.4	
			35 °C		
			A_e	4.9E-05	mol/g
			k	0.25	1/min
			pH	3.2-3.3	
40 °C			**40 °C**		
A_e	9.6E-05	mol/g	A_e	4.6E-05	mol/g
k	0.61	1/min	k	0.25	1/min
pH	4.1-4.9		pH	3.3-3.5	

Our previous studies [25] revealed that the iron (III) ions sorbed on bentonite produce iron oxide hydroxide compounds in the interlayer spaces. Moreover, the sorbed amount of iron (III) exceeds the cation exchange capacity suggesting that these compounds can be present on the outer surfaces. The iron (III) oxide hydroxide compounds can sorb the phosphate more easily than interlayer rare earth cations.

3.3 Isotherms of phosphate on modified bentonites

The isotherm of phosphate on Y-bentonites is presented in Fig. 5. Similar figures were obtained for the other modified bentonites. The corresponding isotherm parameters were obtained by plotting ce/a (g/dm^3) versus ce (mol/dm^3), where a_e is the amount adsorbed at equilibrium (mol/g), c_e is the equilibrium solution concentration (mg/l). The sorption of phosphate on modified bentonites reaches equilibrium at about 1 h.

Under the same experimental conditions, La-, Ce- and Y-bentonites can bind similar amount of phosphate ions. Iron (III) bentonite, despite its high numbers of active sites binded only half much phosphate as La-, Ce-, and Y-bentonite. The high solubility of the bentonite-phosphate-iron(III) complex inhibits the phosphate sorption in some degree.

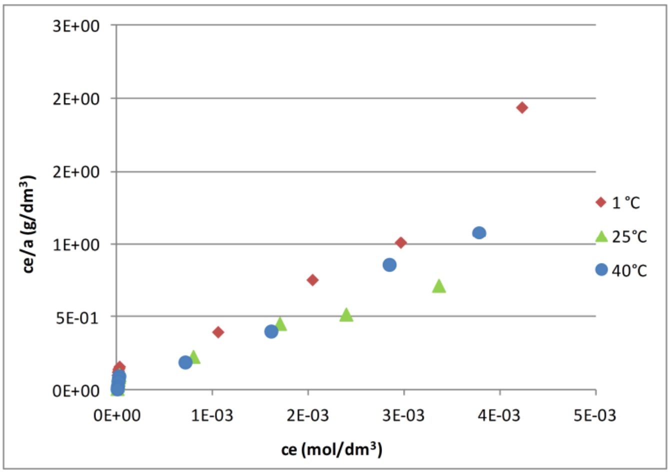

Fig. 5 Phosphate sorption isotherms at 1 °C, 25 °C and 40 °C in Y modified bentonite, 100 mg bentonite, 20 cm^3 KH_2PO_4, pH 4.2-5

The number of active sites (Table 4) on La-, Ce- and Y-bentonite is nearly equal.

The solubility of the sorption complex (rare earth ion-phosphate-bentonite) (Table 4) decreases as the temperature increases. The tendencies of active sites and solubility vs time are similar to rare earth bentonites, showing the exothermic phosphate sorption reaction.

Table 4 Isotherm parameters for phosphate sorption on modified bentonites

La-bentonite			Ce-bentonite		
T	active sites	solubility	T	active sites	solubility
	mol/g	mol/dm^3		mol/g	mol/dm^3
1 °C	2.68E-04	1.73E-05	*1* °C	4.35E-04	4.65E-05
25 °C	2.02E-04	1.55E-06	25 °C	1.99E-04	2.25E-06
40 °C	2.42E-04	4.94E-06	40 °C	1.99E-04	1.67E-06
Y-bentonite			Fe-bentonite		
T	active sites	solubility	T	active sites	solubility
	mol/g	mol/dm^3		mol/g	mol/dm^3
1 °C	3.81E-04	3.01E-05	*1* °C	1.77E-03	3.54E-04
25 °C	2.12E-04	2.97E-06	25 °C	1.68E-03	3.40E-04
40 °C	2.03E-04	1.62E-06	40 °C	4.41E-04	6.75E-05

The number of active sites is the highest at 1 °C and is in a good agreement with the rare earth concentration of the modified bentonite, proving the $REEPO_4$ (rare earth ion-phosphate) surface precipitation mechanism. This suggests an exothermic surface precipitation process. It is interesting to note that the solubility of some phosphate precipitates changes just at the same way [26].

3.4 Desorption of phosphate on modified bentonites

Based on the measurements, a negligible amount of phosphate was dissolved during desorption.

4 Conclusion

Four modified bentonites (La, Ce, Y, and Fe(III)) were applied to remove phosphate ions from aqueous solution. The kinetics, equilibrium time, sorption isotherms were examined.

The activation energy (E_a) of phosphate sorption on rare earth bentonites varied between 22-37 kJ/mol.

Phosphate ions sorb in the interlayer space as $REEPO_4$.

The activation energy of phosphate sorption on iron (III) modified bentonite is less than that of rare earth bentonite, namely 10 kJ/mol.

Under the same experimental conditions, La-, Ce- and Y-bentonites can bind similar amount of phosphate ions, while iron only half much phosphate as La-, Ce-, and Y-bentonite.

A negligible amount of phosphate was dissolved during desorption. Examination about enhancement and re-use of the sorbents will be carried out.

These results show that modified clays could play an important role in the treatment of eutrophication processes in the aquatic environment. Ce-oxide is 2.5 times cheaper than La-oxide. Fe(III)-chloride is 25 times cheaper than La-oxide. Preparation of these two modified bentonite is more economical.

Acknowledgement

The project presented in this article is supported by the EU and co-financed by the European Regional Development Fund under the project GINOP-2.3.2-15-2016-00008. The work was supported by the Hungarian National Research, Development, and Innovation Office (NKFIH K 120265). The authors thank dr. Klara Dufresne for the improvement of English.

References

[1] Waajen G., Oosterhout van F., Douglas G., Lürling M. "Management of eutrophication in Lake De Kuil (The Netherlands) using combined flocculant – Lanthanum modified bentonite treatment." *Water Research*. 97, pp. 83–95. 2016. https://doi.org/10.1016/j.watres.2015.11.034

[2] Wendling L. A., Blomberg P., Sarlin T., Priha O., Arnold M. "Phosphorus sorption and recovery using mineral-based materials:Sorption mechanisms and potential phytoavailability." *Applied Geochemistry*. 37, pp. 157–169. 2013. https://doi.org/10.1016/j.apgeochem.2013.07.016

[3] Sutcliffe, D.W., Jones, J.G. "*Eutrophication Research and Application to Water Supply*." Freshwater Biological Association, pp. 4–29 Ambleside, London, UK, 1992

[4] Pieterse, N. M., Bleuten, W., Jørgensen, S. E. "Contribution of point sources anddiffuse sources to nitrogen and phosphorus loads in lowland river tributaries." *Journal of Hydrology*. 271, pp. 213–225. 2003. https://doi.org/10.1016/S0022-1694(02)00350-5

[5] Jarvie, H. P., Neal, C., Withers, P. J. A. "Sewage-effluent phosphorus: a greater riskto river eutrophication than agricultural phosphorus?" *Science of the Total Environment*. 360, pp. 246–253. 2006. https://doi.org/10.1016/j.scitotenv.2005.08.038

[6] Xue, Y., Hou, H., Zhu, S. "Characteristics and mechanisms of phosphate adsorption onto basic oxygen furnace slag." *Journal of Hazardous Materials*. 162, pp. 973–980. 2009. https://doi.org/10.1016/j.jhazmat.2008.05.131

[7] Sen, T. K., Gomez, D. "Adsorption of zinc (Zn^{2+}) from aqueous solution on natural bentonite." *Desalination.* 267, pp. 286–294. 2011. https://doi.org/10.1016/j.desal.2010.09.041

[8] Gibbs, M., Hickey, C.W., Özkundakci, D. "Sustainability assessment and comparison of efficacy of four P-inactivation agents for managing internal phosphorus loads in lakes: sediment incubations." *Hydrobiologia.* 658, pp. 253-275. 2011. https://doi.org/10.1007/s10750-010-0477-3

[9] Zamparas, M., Gianni, A., Stathi, P., Deligiannakis, Y., Zacharias, I. "Removal of phosphate from natural waters using innovative modified bentonites." *Applied Clay Science*. 62-63, pp. 101-106. 2012. https://doi.org/10.1016/j.clay.2012.04.020

[10] Haghseresht, F., Wang, S., Do, D. D. "A novel lanthanum-modified bentonite, Phoslock, for phosphate removal from wastewaters." *Applied Clay Science*. 46, pp. 369–375. 2009. https://doi.org/10.1016/j.clay.2009.09.009

[11] Genz, A., Kornmüller, A., Jekel, M. "Advanced phosphorus removal from membrane filtrates by adsorption on activated aluminium oxide and granulated ferric hydroxide." *Water Research*. 38, pp. 3523–3530. 2004. https://doi.org/10.1016/j.watres.2004.06.006

[12] Georgantas, D. A., Grigoropoulou, H. P. "Phosphorus removal from synthetic and municipal wastewater using spent alum sludge." *Water Science and Technology*. 52, pp. 525–532. 2005

[13] Carabante, I., Grahn, M., Holmgren, A., Hedlund, J. "In situ ATR–FTIR studies on the competitive adsorption of arsenate and phosphate on ferrihydrite." *Journal of Colloid and Interface Science*. 351, pp. 523–531. 2010. https://doi.org/10.1016/j.jcis.2010.07.064

[14] Zeng, L., Li, X., Liu, J. "Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings." *Water Research*. 38, pp. 1318–1326. 2004. https://doi.org/10.1016/j.watres.2003.12.009

[15] Delaney, P., McManamon, C., Hanrahan, J. P., Copley, M. P., Holmes, J. D., Morris, M. A. "Development of chemically engineered porous metal oxides for phosphate removal." *Journal of Hazardous Materials*. 185, pp. 382–391. 2011. https://doi.org/10.1016/j.jhazmat.2010.08.128

[16] Karapinar, N. "Application of natural zeolite for phosphorus and ammonium removal from aqueous solutions." *Journal of Hazardous Material.s* 170, pp. 1186–1191. 2009. https://doi.org/10.1016/j.jhazmat.2009.05.094

[17] Nagy, N. M. Kónya, J. "*Interfacial Chemistry of Rocks and Soils*." pp. 83-117,CRC Press, Taylor and Francis Group, New York, USA, 2009.

[18] Li, J., Li, Y., Meng, Q. "Removal of nitrate by zero-valent iron and pillared bentonite." *Journal of Hazardous Materials* 174, pp. 188–193. 2010. https://doi.org/10.1016/j.jhazmat.2009.09.035

[19] Kuzmann, E., Singh, L. H., Garg, V. K., de Oliveira, A. C., Kovács, E. M., Molnár, Á. M., Homonnay, Z., Kónya, P., Nagy, N. M., Kónya, J. "Mössbauer study of the effect of rare earth substitution into montmorillonite." *Hyperfine Interaction*. 237, p. 2. 2016. https://doi.org/10.1007/s10751-016-1225-5

[20] Richards, L. A. "*Diagnosis and Improvement of Saline and Alkaline Soils*." U.S. Dept. Agr. Handbook, 60, 1957.

[21] Tong-Shuang, L., Zhan-Hui, Z., Yong-Jian, G. "A rapid preparation of acylals of aldehydes catalysed by Fe^{3+} -montmorillonite." *Synthetic Communications*. 28, pp. 4665-4671. 1998. https://doi.org/10.1080/00397919808004531

[22] Murphy, J., Riley, J. P. "A modified single solution method for the determination of phosphate in natural waters." *Current Contents/Agriculture Biology & Environmental Sciences*. 12, pp. 16-16. 1986.

[23] Chubar, N. I., Kanibolotskyy, V. A., Strelko, V. V., Gallios, G. G., Samanidou, V. F., Shaposhnikova, T. O., Milgrandt, V. G., Zhuravlev, I. Z. "Adsorption of phosphate ions on novel inorganic ion exchangers." *Colloids and Surfaces A Physicochemical and Engineering Aspects*. 255, pp. 55–63. 2005. https://doi.org/10.1016/j.colsurfa.2004.12.015

[24] Karaca, S., Gürses, A., Ejder, M., Acikyildiz, M. "Adsorptive removal of phosphate from aqueous solutions using raw and calcined dolomite." *Journal of Hazardous Materials.* 128, pp. 273–279. 2006. https://doi.org/10.1016/j.jhazmat.2005.08.003

[25] Komlósi, A., Kuzmann, E., Nagy, N. M., Homonnay, Z., Kubuki, S., Kónya, J. "Interlayer incorporation of iron into Na-bentonite via treatment with $FeCl_3$ in acetone." *Clays and Clay Minerals*. 55, pp. 91-97. 2007. https://doi.org/10.1346/ccmn.2007.0550107

[26] Firsching, F. H., Brune, S. N. "Solubility Products of the Trivalent Rare-Earth Phosphates." *Journal of Chemical and Engineering Data*. 36, pp. 93-95. 1991. https://doi.org/10.1021/je00001a028