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A Review of the Role of Natural Clay Minerals as Effective Adsorbents and an Alternative Source of Minerals

Aref Alshameri, Xinghu Wei, Hailong Wang, Yang Fuguo, Xin Chen, Hongping He, Chunjie Yan and Feng Xu

Abstract

The minerals with unique properties such as natural clay minerals (NCMs) have promising approach in environmental and industrial sphere. In fact, under some specific conditions the NCMs could be used either as effective adsorbent material or alternative source of minerals. This chapter presents an outline of a general review of factors that affect the application ability of NCMs and a descriptive analysis of NH_4^+ and REE adsorption behavior and extraction of rare earth elements (REE) by an ion-exchange with NH_4^+ ions onto NCMs. Clays and NCMs both effectively remove various contaminants from aqueous solution and serve as alternative sources of minerals, as extensively discussed in this chapter. This review compiles thorough literature of current research and highlights the key findings of adsorption (NH_4^+ and REE) that use different NCMs as adsorbents or alternative sources of minerals (i.e., REE). The review confirmed that NCMs excellently remove different cations pollutants and have significant potential as alternative source of REE. However, modification and further development of NCMs applications for getting the best adsorption and the best extraction of REE onto NCMs, which would enhance pollution control and leaching system is still needed.

**Keywords:** natural clay minerals, adsorption mechanism, ammonium, rare earth elements, REE extraction

1. Introduction

Natural clay minerals (NCMs) have gained considerable attention due to their unique properties and their use in huge range of industrial and environmental applications [1, 2]. NCMs are unique in the sense that these minerals are studied by, and used in, many disciplines for essential and applied research [3, 4]. These minerals are nontoxic to ecosystem and play important role in the development of human civilization. They have been utilized in agricultural applications, engineering and construction applications, environmental remediation, geology, pharmaceuticals, food processing and many other industrial applications [2, 5]. The economic benefits look evident due to the fact that NCMs are widespread, and inexpensive compared with other raw materials [6]. For these reasons, NCMs research is being actively pursued by many scientists and in several countries, and the future of clay science seems exciting, and promising.

1.1. Structure and composition of the NCMs

NCMs can arguably be considered as phyllosilicate class, containing layered structures of shared octahedral aluminum and tetrahedral silicon sheets, water molecules and hydrated cations that can move in and out of the interlayer spaces [7, 8]. Commonly, isomorphous substitution of one cation with another (of similar size but with lesser charge, such as Al^{3+} for Si^{4+} or Mg^{2+} for Al^{3+}) within crystal structures leads to a charge imbalance in silicate NCMs, which accounts for the permanent negative charge on NCMs particles, hence the ability of clays to attract cations to the surface. Amphoteric▬OH groups at the surface/edge of clays (i.e., silanol and aluminol groups) could also contribute to surface charge (pH-dependent reversible charge).

The physical and chemical properties of any particular NCMs are structure and composition dependent. A general review of the structure and composition of the various NCMs are essentially hydrous aluminum silicates that sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths, and other cations found on or near some planetary surfaces [9]. The atomic structure of NCMs consists of two basic units, an octahedral sheet and a tetrahedral sheet. The octahedral sheet is comprised of closely packed oxygens and hydroxyls in which aluminum, iron, and magnesium atoms are arranged in octahedral coordination (**Figure 1a**). The second structural unit is the silica tetrahedral layer in which the silicon atom
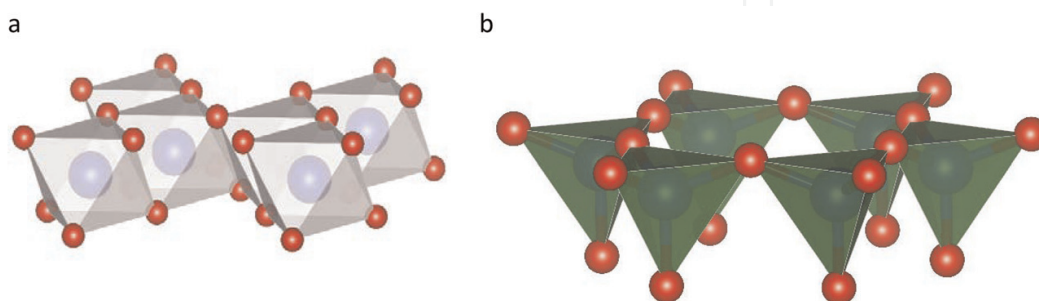
Figure 1. Diagrammatic sketch of the octahedral (a) and the tetrahedral sheet (b).

is equidistant from four oxygens or possibly hydroxyls arranged in a tetrahedron with the silicon atom in the center (**Figure 1b**). NCMs are usually classified based on their structure and layer type [10]. The classification of Grim becomes the basis for outlining the nomenclature and the differences between the various NCMs [3]. Although, it is not possible to compress the discussion of structure and classification of NCMs in this chapter, a simple classification of NCMs is available in literatures, NCMs can be divided into four main groups: kaolinite group, illite group, smectite group, and vermiculite group.

The structure and composition of the major industrial NCMs are different even though they are each comprised of octahedral and tetrahedral sheets as their basic building blocks. The arrangement and composition of the octahedral and tetrahedral sheets account for most of the differences in their physical and chemical properties. Therefore, for their applications an understanding of the structure, physical and chemical properties attributes of the individual clay minerals is important. The huge variety of physical and chemical properties of NCMs provides unlimited scope for future application, particularly in environment protection or as minerals resources. A general review of the structure and composition of the NCMs are given in this chapter. A more detailed discussions of the structures of the various NCMs were discussed in literature [5, 9–13].

1.2. Properties and factors that affect the application ability of natural clay minerals

The use of NCMs for specific applications depends on its type of structure (1.1 or 2.1 layer type) and on its chemical composition [14]. The identity of all the material present in NCMs should be determined in order to evaluate their properties. The most important characteristic of NCMs is the cation exchange capacity (CEC). CEC is to measure the capacity of NCMs to exchange cations from the solution [15], which depends on the volume of the total layer charge. Since the surface layer charge is the function of pH, thus, CEC also changes with pH and regularly CEC is measured at pH 7 [16, 17]. The popular metallic cations found in exchange positions in NCMs are Ca^{2+}, Mg^{2+}, Na^+, and K^+. The presence of charge in NCMs play important role for cation exchange and the swelling properties of the minerals. The hydrolysis of Si━OH or Al━OH bonds along the NCMs lattices supplies the surface charge. Depending on the silica structure and the solution pH, the net surface charge can be either positive or negative. The tetrahedral and octahedral sheets of NCMs usually have a charge. The charge in the NCMs occurs in two forms: structural and surface charge. The structural charge is permanent and present due to ion substitutions, which arises inside the interior of the layers. The surface charges, generally in NCMs depend on the pH value, with 2:1 layer, the surface charge creates on the basal surface of the tetrahedral sheets while the surface charge for layer type 1:1, derives from both of tetrahedral and octahedral sheets. Also, the edges of both 1:1 and 2:1 layer contribute to the surface charge [16]. Several books have explained the details of the structure and properties of NCMs such as Handbook of Clay Science, edited by Bergaya et al. [13].

Furthermore, the presence of amount of exchangeable ions, non-NCMs, soluble salts, and quality of their texture are factors which can affect their properties and applications. The presence of cations in octahedral sheet, and isomorphic substitutions in the octahedral and tetrahedral sheets result in net charge deficits. Varying according to the sheet unit, and

ultimately, in different mineral phases giving rise to varied technical behavior. The textural differences between structurally and chemically identical NCMs also affect their adsorptive properties [15, 17, 18].

The type and amount of non-clay minerals are present with NCMs affect their properties and applications. Non-clay minerals commonly associated with the NCMs include quartz, feldspar, mica, calcite, dolomite, opal C-T, and minor amounts of heavy and trace minerals such as ilmenite, rutile, brookite, anatase, leucoxene, sphene, tourmaline, zircon, kyanite, goethite, hematite, magnetite, garnet, augite, florencite, apatite, andalusite, and barite. Subsequently, when developing applications for NCMs, it is necessary to take these factors into consideration. It is important to know the specific properties of NCMs one is using in order to ensure that it is appropriate for one's needs or to better understand their mechanism behavior during experimental process.

1.3. Techniques of NCMs characterization

There is increasing trend in the popularity of productive research in the field of NCMs. Characterization of NCMs is given significance as they are mainly used as cation exchangers, sorbents/hosts, and catalysts. Usually, the characterization of a number of techniques has to be done in order to get comprehensive details of the NCMs.

Moreover, the multitude of techniques also accelerates the process of development of NCMs, particularly as catalysts, as different aspects are discovered. Extensive research in the field of instrumentation has resulted in advanced techniques of analysis that have helped in characterization of molecular sieves in general and NCMs in particular. In common, the characterization of NCMs should provide information about; (i) chemical composition; (ii) structure and morphology; (iii) ability to adsorb and retain molecules, and (iv) ability to chemically convert these molecules.

The techniques for NCMs characterization, include X-ray diffraction (XRD), transmission electron microscopy (TEM), electron-beam-based microscopy, scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX), Fourier transform infrared (FTIR) spectroscopy, X-ray fluorescence (XRF), magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy (MASNMR), X-ray photoelectron spectroscopy (XPS) analyses, N_2 adsorption-desorption isotherms and zeta potential analysis to obtain the mineralogical and physicochemical parameters.

XRD is generally used to identify the presence and quantitative determination of crystalline NCMs. SEM is useful for morphological analysis and chemical analyses at specific locations. The chemical compositions are determined using XRF. IR and NMR provide insight into acid sites and framework structure. It is not possible to compress the discussion of such techniques and research done on their scope and development. Literatures provide useful insight into various characterization techniques for NCMs [5, 13, 15].

Here, we compile research data from various publications related to the use of different NCMs-based adsorbents and the leaching technology generations for REE extraction, notably

thorough literature of our current researches. In the first part of this chapter, general structure, properties and the factors that affect the application ability of NCMs are discussed. The techniques of NCMs characterization are also summarized. The main goal of this review is to explain why an understanding of the structure and surface properties of the individual NCMs are so important. This chapter provides an elaborate information about the different NCMs as effective adsorbents in environment protection and their importance for the extraction of rare earth elements in ion adsorption clays. It has also adequately summarized the role of factors that affect adsorption (i.e., NH_4^+ and REE) and extraction behavior of REE onto NCMs.

2. Adsorption behavior of contaminants and recovery of rare earth elements adsorbed on natural clay minerals

In environment protection, NCMs have been used in the elimination and storage of hazardous chemicals [14, 19, 20]. NCMs have the catalytic capability to neutralize certain organic hazardous chemicals [15, 20, 21]. The ability of NCMs to contain hazardous substances depends on their cation exchange capacity (CEC) while the process of retaining toxic materials mainly occurs by the ion exchange and/or adsorption. Due to their high cation exchange capacity, NCMs are very effective for the adsorption of cations from the solution. Although the NCMs are electronegatively charged [22], these minerals still can adsorb organic and non-ionic substances in significant amounts. The adsorption characteristics are dependent upon the chemical/structural makeup of the adsorbent, the Si/Al ratio, cation type; number and location are particularly influential in adsorption. The adsorption capacity of NCMs can be improved by modification with inorganic salts ($NaCl$, $CaCl_2$, $BaCl_2$, NH_4Cl, $AlCl$, $FeCl_3$), cationic surfactants, acid, base and organic [23, 24]. Consequently, the NCMs become hydrophobic and organophilic, which led to the enhancement of the adsorption of non-ionic and organic compounds [25, 26]. Notably, in our brief studies of NH_4^+ and REE adsorption, we used nonmodified NCMs, to better understand the natural system reactivity of NCMs, and also the modification of natural minerals at a larger scale may increase the processing cost; thus, reliable water treatment by using non-modified clay minerals is highly desirable. Therefore, utilization of NCMs would solve disposal problem, and also access to inexpensive materials in the wastewater treatment. Moreover, due to low cost of NCMs, there is no need to regenerate them; which provide more advantages in using NCMs as an adsorbent materials.

2.1. A brief review of adsorption of NH_4^+

Nitrogen compounds in aqueous environments are commonly found in the form of ammonium ions (NH_4^+). Important sources of NH_4^+ include effluent from the application in agricultural practices and industrial processes resulting in algal bloom in lakes and rivers [27, 28]. NH_4^+ concentration, in certain surface waters serving as a source of potable water, is much higher than the permissible level, due to large quantities of industrial and municipal wastewater being discharged into existing water resources [29–31]. Also, the NH_4^+ concentration for most fish species must not exceed 1.5 mg [32, 33]. Therefore, complete removal of NH_4^+ is required due to its toxicity to the majority of aquatic lives.

For these reasons, the prevention of nitrogen pollution with NH_4^+ removal from wastewater is of great importance [34–36]. Various methods including air stripping, biological methods and activated carbon have been used for NH_4^+ removal [37]. However, these techniques are not suitable for use in the removal of low contaminants concentrations, which cause damage both to the environment and life [31]. Additionally, high costs, poor regeneration and uncertainty of outcome are some of the frequently encountered limitations in the application of these methods [36, 38, 39]. Furthermore, contingency on temperature and climate conditions constitutes another disadvantage in this process.

Compared with the above mentioned methods, high safety, low cost [34, 40, 41] and relative simplicity of application and operation are some of the attributes that are attracting an increasing focus on the use of adsorption method for environment applications [33, 42, 43]. Adsorption process is a suitable technique for pollutants removal from wastewater, because of the significant advantages like low-cost, profitability, availability, and effectiveness than other methods. This method is easy to operate and equally effective in the removal of toxic contaminants, even at low concentrations [44].

2.1.1. Investigations of NH_4^+ adsorption properties of six natural clay minerals

This research presented six types of NCMs-based adsorbents namely kaolinite, halloysite, montmorillonite, vermiculite, palygorskite, and sepiolite were examined and compared in the same study [44]. The study illustrated that among all the NCMs studied, vermiculite and montmorillonite have the highest ammonium adsorption capacities. The study revealed that the cation exchange is the main mechanism for the NH_4^+ adsorption. Negatively charged surface, specific surface area, water absorption process and surface morphology of NCMs might also contribute to the high adsorption capacities. Adsorption kinetics showed that the adsorption behavior followed the pseudo-second-order kinetic model whereas the isotherms fitted the Langmuir model. The insights obtained in this study are useful for applications of NCMs in environmental remediation. The results illustrated that the structure and surface properties of NCMs are the key factors that affect the adsorption capacities for NH_4^+. The study concluded that the NCMs have significant potential as economic, safe and effective adsorbent materials for the NH_4^+ adsorption from the aqueous solution at low concentrations.

2.2. A brief review of adsorption/extraction of rare earth elements

2.2.1. Adsorption of rare earth elements (REE)

REE group consists of 17 elements and is divided into two categories namely the light rare earths (L-REE) and the heavy rare earths (H-REE). REE have been used widely in metallurgy, chemical engineering, electronics and electrooptics, medicine, biomedicine, for manufacturing of magnetostriction materials and lasers [45–47]. Its applications in advanced technologies are increasing [48]. In modern societies, the rare earth elements (REE) are considered because of their unique physical and chemical properties. REE will be of substantial attention for the foreseeable future, with demand likely to grow.

Therefore, due to the increasing use of REE in industries, determination of REE has been of a recent increasing concern. Several analytical techniques were used to determine REE in samples such as inductively coupled plasma-mass spectrometry (ICP-MS) [49], neutron activation (INAA) [50]. Energy dispersive X-ray fluorescence (EDXRF) [51] and inductively coupled plasma optical emission spectroscopy (ICP-OES) [52]. Research should continue to play an important role in the search for rare earth ore deposits and their extraction, ensuring that as little damage is done to the environment as conceivable.

Various techniques have been used for removal of REE ions from aqueous systems such as solid-phase extraction, solvent extraction, ion exchange, ion-selective electrodes [53–59] and adsorption [60–62]. Adsorption method is the best technique because of low cost, simplicity of design and operation. The ion-adsorption type rare earths ore, is mainly located in China and REE in these deposits were released by weathering of REE-rich granites and subsequently adsorbed by NCMs.

Recently, there has been a significant interest in adsorption of rare earth elements with NCMs [1, 63–65]. Piasecki and Sverjensky [66] also had studied REE speciation/distribution on wide ranges of pH and ionic strength. They concluded that most of the surface-adsorbed lanthanides occur as simple "clay-REE" or as hydrolyzed "clay-O-REE^{2+}" species.

NCMs are electronegative, saturated with cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+} are capable of exchanging cations such as REE to the surface. Previous researches have shown that REE contained in NCMs are mainly present as physisorbed ions, which can be easily recovered by a simple ion-exchange procedure [66, 67]. It is evident that the adsorption of REE ions on NCMs would have great influence on the mineralization process and the leaching process of the ion-adsorption type rare earths ore.

2.2.2. Extraction of REE from ion adsorption clays

The ion-adsorption type rare earths ore are generally formed by weathering of REE rich host rocks (granitic or igneous) and transfer into an aqueous solution which percolates through the weathering body and are adsorbed onto NCMs [68–71]. This provides evidence that NCMs have the ability of adsorbing lanthanide ions released/solubilized during weathering [72]. However, although, the NCMs deposits containing adsorbed lanthanides which are of substantially lower grade than other types of REE mineral resources, the economic benefits look remarkable, because NCMs are abundant in surface layers in nature, easier ionic exchange of REE, ease of mining and processing [66, 73]. It is thus evident that the adsorption of rare earth ions on NCMs would have great influence on the mineralization process and the leaching process of the ion-adsorption type rare earths ore.

During the past 45 years, the leaching technology in REE extraction were investigated [64, 74, 75]. The extraction of REE has been a long tradition in China using the concept of ion-exchange leaching. In the ion adsorption clays 60–90% of the REE are adsorbed onto NCMs [71] and the adsorbed REE on NCMs could be easily recovered by leaching with monovalent salt solutions. Recently, the ion-adsorption rare earth ores have the focus of most research endeavors as an

alternative source of REE, the results of leaching efficiencies has been reported [66, 71, 73, 75, 76]. Based on these findings, $(NH_4)_2SO_4$ was identified as the best a lixiviant of REE from NCMs.

2.2.3. Investigations of adsorption/extraction behavior for REE onto natural clay minerals

Four natural clay minerals namely kaolinite, montmorillonite, muscovite and illite were systematically investigated and compared for their adsorption/extraction behavior for REE [77]. The study reported that the montmorillonite exhibits highest adsorption and regeneration efficiencies for REE while kaolinite has highest extractions efficiencies for both REE light and heavy in the order of kaolinite > illite > montmorillonite > muscovite. Also study found that the lack extractions of REE from muscovite than other NCMs are believed to presence of iron oxide and biotite mineral (produce iron oxide as a result of its alteration) associated with muscovite. The leaching process of the REE is a kind of the reversibility of the ion-exchange process, it was evident that the cation exchange and negatively charged surfaces are the mechanism for REE adsorption. It was concluded that NH_4^+ is lacking as a lixiviant from NCMs since NCMs are associated with iron oxide, particularly, either with NCMs containing iron (i.e., biotite) or minerals which always associate with biotite such as muscovite. The important role of the pH in extraction of REE from NCMs was evidenced, when REE-NCMs come into contact with the NH_4^+ solution, the pH is rapidly increased from the initial pH solution for both montmorillonite and muscovite, leading to the decrease of the availability of ion-exchangeable REE with NH_4^+ ions. That is one of the factors that influence the reduction in the REE extraction from montmorillonite and muscovite when compared with those of kaolinite and illite. The results illustrated that the structure and surface properties of NCMs are also the key factors that affect the rare earth leaching, consequently identifying the types of NCMs and associated impurities in clay materials is important for getting the best leaching system [77].

3. Conclusion

NCMs have gained a significant interest among the scientific community, because of their abundance, low cost and their unique properties. In this regard, a systematic comparison study under identical experimental conditions could help to better understand the influence of structure and properties of NCMs on their adsorptive/extraction behaviors towards contaminants and elements in leaching process. Adsorption is a very promising and efficient technology for the removal of hazardous contaminants from water source, thus NCMs have been successfully used as an adsorbent materials and alternative source of minerals. Batch adsorption experiments have demonstrated that the contact time, initial pollutants concentration, adsorbent dosage and solution pH have significant effects on contaminants adsorption/desorption. Among all the NCMs studied, montmorillonite and vermiculite exhibit the highest adsorption efficiencies towards NH_4^+ and REE. The presence of iron oxide with NCMs found to help enhance REE adsorption (REE-Fe-oxides), meanwhile it also influences the extraction of REE because REE-Fe-oxides cannot be easily recovered by monovalent salt solutions using the

concept of ion exchange i.e., NH_4^+. The structure and surface properties of NCMs are the key factors that affect the adsorption capacities for contaminants and extraction of minerals (i.e., REE). The review suggests that NCMs can be considered as ideal adsorbents and alternative source of minerals owing to their low cost, abundant, high safety, and good adsorption efficiencies. Identifying the types of NCMs and associated impurities in clay materials is important either for getting the best adsorption or the best leaching system. Thus, when developing applications for NCMs, it is essentially to take these factors into consideration. However, further study is necessary to establish the process parameters to generate better quality of products. Also, modification and thermal treatment of natural clay minerals could provide potential future applications in water treatment.

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References

[1] Anastopoulos I, Bhatnagar A, Lima E. Adsorption of rare earth metals: A review of recent literature. Journal of Molecular Liquids. 2016;**221**:954-962. DOI: 10.1016/j.molliq.2016.06.076

[2]   Reyes C, Fiallo L. Application of illite-and kaolinite-rich clays in the synthesis of zeolites for wastewater treatment. In: Imran Ahmad Dar (ed.), Earth and Environmental Sciences. Rijeka, Croatia: Intech Open; 2011. p. 234-246. DOI: 10.5772/25895

[3]   Grim R. Applied Clay Mineralogy. New York, USA: McGraw-Hill Book Company; 1962. 6d. DOI: 10.1080/11035896209447314

[4]   Su L, Zeng X, He H, Tao Q, Komarneni S. Preparation of functionalized kaolinite/epoxy resin nanocomposites with enhanced thermal properties. Applied Clay Science. 2017;**148**: 103-108. DOI: 10.1016/j.clay.2017.08.017

[5]   Murray H. Applied Clay Mineralogy. Developments in Clay Science. 1st ed. Amsterdam: Elsevier; 2006. 188p. DOI: 10.1016/S1572-4352(06)02001-0

[6]   Sabino D, Giusy L, Mariangela G, Michele N. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. Sustainable Materials and Technologies. 2016;**9**:10-40. DOI: 10.1016/j.susmat.2016.06.002

[7]   Sposito G, Skipper N, Sutton R, Park S, Soper A, Greathouse J. Surface geochemistry of the clay minerals. Proceedings of the National Academy of Sciences. 1999;**96**:3358-3364. DOI: 10.2307/47645

[8]   Bergaya F, Lagaly G. Hand Book of Clay Science, General Introduction: Clays, Clay Minerals, and Clay Science. Developments in Clay Science. Amsterdam: Elsevier; 2013. p.19. DOI: 10.1016/B978-0-08-098258-8.00001-8

[9]   Bergaya F, Lagaly G, editors. Handbook of Clay Science. Developments in Clay Science. Amsterdam: Elsevier; 2006. 1224 pp

[10] Brigatti F, Galan E, Theng B. Structures and mineralogy of clay minerals. In: Developments in Clay Science. Amsterdam: Elsevier; 2006. pp. 19-86. DOI: 10.1016/S1572-4352(05) 01002-0

[11] Bailey S. Chlorites; structures and crystal chemistry. Reviews in Mineralogy and Geochemistry. 1988;**19**:347-403. DOI: 10.1515/9781501508998-015

[12] Moore D, Reynolds R. X-Ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford: Oxford University Press; 1989. 322 pp. DOI: 10.1180/claymin.1990.025.4.11

[13] Bergaya F, Lagaly G. General introduction: Clays, clay minerals, and clay science. Developments in Clay Science. 2006;**1**:1-18. DOI: 10.1016/S1572-4352(05)01001-9

[14] Zadinelo I, José Alves H, Moesch A, Colpini L, Silva L, Santos L. Influence of the chemical composition of smectites on the removal of ammonium ions from aquaculture effluents. Journal of Materials Science. 2015;**50**:1865-1875. DOI: 10.1007/s10853-014-8749-3

[15] Ismadji S, Soetaredjo F, Ayucitra A. Clay Materials for Environmental Remediation. Cham: Springer; 2015. DOI: 10.1007/978-3-319-16712-1

[16] Eslinger E, Pevear D. Clay Minerals for Petroleum Geologists and Engineers. SEPM Short Course Notes no 22, ix + 405 pp. Society of Economic Paleontologists and Mineralogists. Tulsa; 1988. OI: https://doi.org/10.2110/scn.88.01

[17] Yuan G, Theng B, Churchman J, Gates W. Clays and clay minerals for pollution control. In: Developments in Clay Science. Amsterdam: Elsevier; 2013. p. 587-644. DOI: 10.1016/B978-0-08- 098259-5.00021-4

[18] Xinggang W, Shaoyu L, Chunmei G, Xiubing X, Xinjie Z, Xiao B, et al. Highly efficient adsorption of ammonium onto palygorskite nanocomposite and evaluation of its recovery as a multifunctional slow-release fertilizer. Chemical Engineering Journal. 2014;**252**:404-414. DOI: 10.1016/j.cej.2014.04.097

[19] Lin S, Juang R. Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review. Journal of Environmental Management. 2009; **90**:1336-1349. DOI: 10.1016/j.jenvman.2008.09.003

[20] Beall G. The use of organo-clays in water treatment. Applied Clay Science. 2003;**24**:11-20. DOI: 10.1016/j.clay.2003.07.006

[21] Uğurlu M, Karaoğlu M. Adsorption of ammonium from an aqueous solution by fly ash and sepiolite: Isotherm, kinetic and thermodynamic analysis. Microporous and Mesoporous Materials. 2011;**139**:173-178. DOI: 10.1016/j.micromeso.2010.10.039

[22] Churchman G, Gates W, Theng B, Yuan G. Chapter 11.1 Clays and clay minerals for pollution control. In: Developments in Clay Science. Vol. 1. Amsterdam: Elsevier; 2006. p. 625-675. DOI: 10.1016/S15724352(05)01022

[23] Seung L, Diwakar T. Organo and inorgano-organo-modified clays in the remediation of aqueous solutions: An overview. Applied Clay Science. 2012;**59-60**:84-102. DOI: 10.1016/j.clay.2012.02.006

[24] Vercellone S, Sham E, Torres E. Measure of zeta potential of titanium pillared clays. Procedia Materials Science. 2015;**8**:599-607. DOI: 10.1016/j.mspro.2015.04.114

[25] Srinivasan R. Advances in application of natural clay and its composites in removal of biological, organic, and inorganic contaminants from drinking water. Advances in Materials Science and Engineering. 2011;**2011**:1-17. DOI: 10.1155/2011/872531

[26] Zaghouane-Boudiaf H, Boutahala M. Kinetic analysis of 2,4,5-trichlorophenol adsorption onto acid-activated montmorillonite from aqueous solution. International Journal of Mineral Processing. 2011;**100**:72-78. DOI: 10.1016/j.minpro.2011.04.011

[27] Wang M, Liao L, Zhang X, Li Z, Zhiguo X, Cao W. Adsorption of low-concentration ammonium onto vermiculite from Hebei Province, China. Clays and Clay Minerals. 2011;**59**:459-465. DOI: 10.1346/CCMN.2011.0590503

[28] Peng X, Xuejing W, Xin W, Jingke S, Hao W, Jing Z, et al. Struvite crystallization combined adsorption of phosphate and ammonium from aqueous solutions by mesoporous MgO–loaded diatomite. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2016;**506**:220-227. DOI: 10.1016/j.colsurfa.2016.05.101

[29] Njoroge B, Mwamachi S. Ammonia removal from an aqueous solution by the use of a natural zeoli. Journal of Environmental Engineering and Science. 2004;**3**:147-154. DOI: 10.1139/s03-070

[30] Yanhui L, Qiuju D, Tonghao L, Xianjia P, Junjie W, Jiankun S, et al. Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon nanotubes. Chemical Engineering Research and Design: Transactions of the Institution of Chemical Engineers. 2013;**91**:361-368. DOI: 10.1016/j.cherd.2012.07.007

[31] Alshameri A, Yan C, Al-Ani Y, Dawood A, Ibrahim A, Zhou C, et al. An investigation into the adsorption removal of ammonium by salt activated Chinese (Hulaodu) natural zeolite: Kinetics, isotherms, and thermodynamics. Journal of the Taiwan Institute of Chemical Engineers. 2014;**45**:554-564. DOI: 10.1016/j.jtice.2013.05.008

[32] Sun Z, Qu X, Wang G, Zheng S, Frost R. Removal characteristics of ammonium nitrogen from wastewater by modified Ca-bentonites. Applied Clay Science. 2015;**107**:46-51. DOI: 10.1016/j.clay.2015.02.003

[33] Sarioglu M. Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite. Separation and Purification Technology. 2005;**41**:1-11. DOI: 10.1016/j.seppur.2004.03.008

[34] Gupta V, Agarwal S, Saleh T. Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. Journal of Hazardous Materials. 2011;**185**:17-23. DOI: 10.1016/j.jhazmat.2010.08.053

[35] Leyva-Ramos R, Monsivais-Rocha J, Aragon-Piña A, Berber-Mendoza M, Guerrero-Coronado R, Alonso-Davila P, et al. Removal of ammonium from aqueous solution by ion exchange on natural and modified chabazite. Journal of Environmental Management. 2010;**91**:2662-2668. DOI: 10.1016/j.jenvman.2010.07.035

[36] Alshameri A, Ibrahim A, Assabri A, Lei X, Wang H, Yan C. The investigation into the ammonium removal performance of Yemeni natural zeolite: Modification, ion exchange mechanism, and thermodynamics. Powder Technology. 2014;**258**:20-31. DOI: 10.1016/j.powtec.2014.02.063

[37] Moradi O, Yari M, Zare K, Marza B, Najafi F. Carbon nanotubes: A review of chemistry principles and reactions. Fullerene Science and Technology. 2012;**20**:138-151. DOI: 10.1080/1536383X.2010.533312

[38] Europea C. IPPC Reference Document on Best Available Techniques in Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector. Sevilla, Espanya: European IPPC Bureau; 2003

[39] Moussavi G, Talebi S, Farrokhi M, Sabouti R. The investigation of mechanism, kinetic and isotherm of ammonia and humic acid co-adsorption onto natural zeolite. Chemical Engineering Journal. 2011;**171**:1159-1169. DOI: 10.1016/j.cej.2011.05.016

[40] Dimirkou A, Doula M. Use of clinoptilolite and an Fe-over exchanged clinoptilolite in Zn^{2+} and Mn^{2+} removal from drinking water. Desalination. 2008;**224**:280-292. DOI: 10.1016/j.desal.2007.06.010

[41] Alshameri A, Abood A, Yan C, Muhammad AM. Characteristics, modification and environmental application of Yemen's natural bentonite. Arabian Journal of Geosciences. 2014;**7**:841-853. DOI: 10.1007/s12517-013-0855-z

[42] Du Q, Liu S, Cao Z, Wang Y. Ammonia removal from aqueous solution using natural Chinese clinoptilolite. Separation and Purification Technology. 2005;**44**:229-234. DOI: 10.1016/j.seppur.2004.04.011

[43] Kurniawan A, Chan G, Lo W, Babel S. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. Science of the Total Environment. 2006;**366**:409-426. DOI: 10.1016/j.scitotenv.2005.10.001

[44] Alshameri A, He H, Zhu J, Xi Y, Zhu R, Ma L, et al. Adsorption of ammonium by different natural clay minerals: Characterization, kinetics and adsorption isotherms. Applied Clay Science. 2018;**159**:83-93. DOI: 10.1016/j.clay.2017.11.007

[45] Greaves M, Elderfield H, Sholkovitz E. Aeolian sources of rare earth elements to the Western Pacific Ocean. Marine Chemistry. 1999;**68**:31-38. DOI: 10.1016/S0304-4203(01)00018-4

[46] Kondo K, Kamio E. Separation of rare earth metals with a polymeric microcapsule membrane. Desalination. 2002;**144**:249-254. DOI: 10.1016/S0011-9164(02)00320-X

[47] Tadjarodi A, Jalalat V, Zare-Dorabei R. Adsorption of La(III) in aqueous systems by N-(2-hydroxyethyl) salicylaldimine-functionalized mesoporous silica. Materials Research Bulletin. 2015;**61**:113-119. DOI: 10.1016/j.materresbull.2014.09.036

[48] Binnemans K, Jones P. Rare earths and the balance problem. Journal of Sustainable Metallurgy. 2015;**1**:29-38. DOI: 10.1007/s40831-014-0005-1

[49] Raut N, Huang L, Aggarwal S, Lin K. Determination of lanthanides in rock samples by inductively coupled plasma mass spectrometry using thorium as oxide and hydroxide correction standard. Spectrochemical Acta Part B Atomic Spectroscopy. 2003;**58**:809-822. DOI: 10.1016/S0584-8547(03)00016-8

[50] Wang Y, Sun J, Chen H, Guo F. Determination of the contents and distribution characteristics of REE in natural plants by NAA. Journal of Radioanalytical and Nuclear Chemistry. 1997;**219**:99-103. DOI: 10.1007/BF02040273

[51] Cornejo-Ponce L, Peralta-Zamora P, Bueno M. Pre-concentration of rare earths using silica gel loaded with 1-(2-pyridylazo)-2-naphthol (PAN) and determination by energy dispersive X-ray fluorescence. Talanta. 1998;**46**(6):1371-1378. DOI: 10.1016/S0039-9140(98)00002-2

[52] Premadas A, Srivastava P. Inductively coupled plasma atomic emission spectrometric determination of lanthanides and Y in various uranium hydrometallurgical products. Journal of Radioanalytical and Nuclear Chemistry. 2002;**251**:233-239. DOI: 10.1023/A: 1014804007992

[53] Ganjali M, Daftari A, Rezapour M, Puorsaberi T, Haghgoo S. Gliclazide as novel carrier in construction of PVC-based La(III)-selective membrane sensor. Talanta. 2003;**59**:613-619. DOI: 10.1016/S0039-9140(02)00573-8

[54] Gupta V, Jain S, Chandra S. Chemical sensor for lanthanum(III) determination using aza-crown as ionophore in poly(vinyl chloride) matrix. Analytica Chimica Acta. 2003;**486**:199-207. DOI: 10.1016/S0003-2670(03)00506-3

[55] Ganjali M, Kiani-Anbouhi R, Shamsipur M, Poursaberi T, Salavati-Niasari M, Talebpour Z, et al. Novel potentiometric PVC-membrane and coated graphite sensors for lanthanum (III). Electroanalysis. 2010;**16**:1002-1008. DOI: 10.1002/elan.200302899

[56] Zhou S, Li X, Shi Y, Alshameri A, Yan C. Preparation, characterization, and Ce(III) adsorption performance of poly (allylamine)/silica composite. Desalination and Water Treatment. 2015;**5**:1321-1334. DOI: 10.1080/19443994.2014.944221

[57] Akhond M, Najafi M, Tashkhourian J. Lanthanum-selective membrane electrode based on 2,2′-dithiodipyridine. Analytica Chemical Acta. 2005;**531**:179-184. DOI: 10.1016/j.aca.2004.09.089

[58] Shamsipur M, Ershad S, Naser S, Esmaeilbeig A, Kia R, Abdolmaleki A. Polymeric membrane lanthanum(III)-selective electrode based on N,N′-adipylbis (5-phenylazo salicylaldehyde hydrazone). Electroanalysis. 2010;**17**:1828-1834. DOI: 10.1002/elan.200503309

[59] Berijani S, Ganjali M, Sereshti H, Norouzi P. A selective modified nanoporous silica as sorbent for separation and preconcentration of dysprosium in water samples prior to ICP-OES determination. International Journal of Environmental Analytical Chemistry. 2012;**92**:355-365. DOI: 10.1080/03067319.2010.551120

[60] Kikuchi T, Nogami M, Suzuki K. Separation performance for trivalent actinides from lanthanides by thiacalix 4 arenes compounds impregnated silica ion-exchanger. Journal of Alloys and Compounds. 2004;**374**:272-276. DOI: 10.1016/j.jallcom.2003.11.101

[61] Perez-Quintanilla D, Del Hierro I, Fajardo M, Sierra I. Cr(VI) adsorption on functionalized amorphous and mesoporous silica from aqueous and non-aqueous media. Materials Research Bulletin. 2007;**42**:1518-1530. DOI: 10.1016/j.materresbull.2006.10.029

[62] Zheng H, Han L, Ma H, Zheng Y, Zhang H, Liu D, et al. Adsorption characteristics of ammonium ion by zeolite 13X. Journal of Hazardous Materials. 2008;**158**:577-584. DOI: 10.1016/j.jhazmat.2008.01.115

[63] Bradbury M, Baeyens B. Sorption of Eu on Na- and Ca-montmorillonites: Experimental investigations and modelling with cation exchange and surface complexation. Geochimica et Cosmochimica Acta. 2002;**66**:2325-2334. DOI: 10.1016/S0016-7037(02)00841-4

[64] Coppin F, Berger G, Bauer A, Castet S, Loubet M. Sorption of lanthanides on smectite and kaolinite. Chemical Geology. 2002;**182**:57-68. DOI: 10.1016/S0009-2541(01)00283-2

[65] Gladysz-Plaska A, Majdan M, Grabias E. Adsorption of La, Eu and Lu on raw and modified red clay. Journal of Radioanalytical and Nuclear Chemistry. 2014;**301**:33-40. DOI: 10.1007/s10967-014-3111-4

[66] Moldoveanu G, Papangelakis V. Recovery of rare earth elements adsorbed on clay minerals: I. Desorption mechanism. Hydrometallurgy. 2012;**117**:71-78. DOI: 10.1016/j.hydromet. 2012.02.007

[67] Moldoveanu G, Papangelakis V. Recovery of rare earth elements adsorbed on clay minerals: II. Leaching with ammonium sulfate. Hydrometallurgy. 2013;**131**:158-166. DOI: 10.1016/j.hydromet.2012.10.011

[68] Shaomei P. The geological characteristics and the prospecting criteria of the granite-weathering crust ion adsorption type Ree deposits in Nanling area, South China. Materials Science Forum. Trans Tech Publication. 1991;**70-72**:33-42. DOI: 10.4028/www.scientific.net/MSF.70-72.33

[69] Aja S. The sorption of the rare earth element, Nd, onto kaolinite at 25°C. Clays and Clay Minerals. 1998;**46**:103-109. DOI: 10.1346/CCMN.1998.0460112

[70] Bao Z, Zhao Z. Geochemistry of mineralization with exchangeable REY in the weathering crusts of granitic rocks in South China. Ore Geology Reviews. 2008;**33**:519-535. DOI: 10.1016/j.oregeorev.2007.03.005

[71] Feng J, Zhou F, Chi R, Liu X, Xu Y, Xu Y. Effect of a novel compound on leaching process of weathered crust elution-deposited rare earth ore. Minerals Engineering. 2018;**129**:63-70. DOI: 10.1016/j.mineng.2018.09.018

[72] Bruque S, Mozas T, Rodriguez A. Factors influencing retention of lanthanide ions by montmorillonite. Clay Minerals. 1980;**15**:413-420. DOI: 10.1180/claymin.1980.015.4.08

[73] Papangelakis V, Moldoveanu G. Recovery of rare earth elements from clay minerals. In: 1st European Rare Earth Resource Conference; 04–07 September 2014; Milos. 2014. pp. 191-202

[74] Sinitsyn V, Aja S, AKulik D, AWood S. Acid-base surface chemistry and sorption of some lanthanides on K$^+$-saturated marblehead illite: I. Results of an experimental investigation. Geochemical et Cosmochimica Acta. 2000;**64**:185-194. DOI: 10.1016/S0016-7037(99)00175-1

[75] Chi R, Zhou Z, Xu Z, Hu Y, Zhu G, Xu. Solution-chemistry analysis of ammonium bicarbonate consumption in rare-earth-element precipitation. Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science. 2003;**34**:611-617. DOI: 10.1007/s11663-003-0031-z

[76] Tian J, Yin J, Chen K, Rao G, Jiang M, Chi R. Extraction of rare earths from the leach liquor of the weathered crust elution-deposited rare earth ore with non-precipitation. International Journal of Mineral Processing. 2011;**98**:125-131. DOI: 10.1016/j.minpro.2010.11.007

[77] Alshameri A, He H, Xin C, Zhu J, Xinghu W, Zhu R, et al. Understanding the role of natural clay minerals as effective adsorbents and alternative source of rare earth elements: Adsorption operative parameters. Hydrometallurgy. 2019;**185**:149-161. DOI: 10.1016/j.hydromet.2019.02.016